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ELEMENTS OF INORGANIC CHEMISTRY

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ELEMENTS

OF

INORGANIC CHEMISTRY

BY

HARRY C. JONES

PROFESSOR OF PHYSICAL CHEMISTRY IN THE
JOHNS HOPKINS UNIVERSITY

SECOND EDITION

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Dedicated to H. B. I.

WHO HAS RENDERED VALUABLE ASSISTANCE

IN PREPARING THE ILLUSTRATIONS

IN THIS WORK

PREFACE

The condition of chemistry to-day differs greatly from that of twenty years ago. Within this period the new physical chemistry has come into existence, and several generalizations have already been reached which affect fundamentally the whole science of chemistry. Some of these can, and, in the opinion of the author, should be introduced very early in the study of the science.

Take the *theory of electrolytic dissociation*, which to-day is as well established as many of our laws of nature: It has shown us that it is the ions and not the atoms which are the active agents chemically. If the student is taught the contrary in the early stages of his work, later this must all be unlearned, and we know how difficult it is to correct first impressions. If we ask the question, why continue to teach chemistry from a purely atomic standpoint after it has been shown not to be in accord with the facts? about the only answer is that it is, perhaps, a little simpler than the chemistry of ions. This reply must, on reflection, be regarded as highly unsatisfactory. If a student can form a conception of an atom as the smallest indivisible particle of matter, would it be very difficult for him to form a conception of an atom carrying an electrical charge? Indeed, it would be no more difficult than to add to the conception of a piece of metal the charge which it carries when electrical energy has been supplied to it, and we do not hesitate in physics to ask him to take this step. Further, since we know that the ion and not the atom or the molecule is the factor which enters into most chemical reactions, we should insist upon it because it is true.

The *effect of mass* on chemical activity is very great, and this should be pointed out early in the study of chemistry. The wide-reaching generalization known as the *law of mass action* may be discussed somewhat later when the metals are studied.

Another highly important generalization whose significance has come to be recognized through physical-chemical investigations, is the *law of Faraday as the basis of chemical valence.* This, as will be seen, places the whole subject of valence upon an exact physical basis, and gives a definite significance and meaning to what has hitherto been dealt with in a rather vague manner.

The present method of treating the subject of general chemistry does not discard in the least the earlier discovered generalizations. The aim has been to add to these older generalizations those more recently brought to light, and to incorporate them as an essential part of the subject. This necessitates a frequent change, which is often fundamental, in our method of dealing with chemical phenomena, and in our conception of chemical reactions; but change has been introduced only where recent generalizations and discoveries have made it necessary, or at least highly desirable, in order to interpret the facts in terms of what to-day we have every reason to believe is true.

The physical properties of substances are treated rather more fully than in the earlier text-books, since the tendency to-day, introduced by physical chemistry, is to bring chemistry and physics more closely together, rather than to separate them as two distinct sciences. The physical properties of a substance are taken up after its chemical properties, in order that the teacher may conveniently omit more or less of this part of the text if the pupil is not sufficiently advanced to properly appreciate its meaning.

The experiments are placed at the ends of chapters rather than in the body of the text or at the end of the book. By this means the text is made continuous and more readable,

and while the student is compelled to review the text in connection with the experiment, he is not so liable to copy it in describing what he has seen and done. If the experiments were placed at the end of the work, the beginner is liable to miss the connection between what he carries out in the laboratory and what he reads in the book.

The problems are introduced after the experiments at the ends of the chapters. In solving these the student is compelled to review much of the text for a third time, and reviews are the only means of becoming really acquainted with a new subject. Portions of my "Principles of Inorganic Chemistry," which were considered to be adapted to the beginner, have been freely introduced into this book. The review of such portions in the larger work will but serve to impress these fundamental facts upon the more advanced student.

In matters of both experiments and problems the teacher must use his judgment as to what should be omitted, if omissions are necessary. This will depend largely upon the time at the disposal of the class, the laboratory facilities, and the state of development of the pupils.

One injunction must be insisted upon at the risk of repeating what is already hackneyed. Never allow a student to perform an experiment in a slip-shod manner, with soiled apparatus poorly set up. Bad habits thus early inculcated, like erroneous conceptions, are lost with difficulty, if lost at all; and a student is injured rather than aided by such work.

The author wishes to express his indebtedness to a large number of friends for valuable suggestions in preparing this book, and especially to Professor Edward Renouf, Dr. J. E. Gilpin, and Dr. F. H. Getman.

HARRY C. JONES.

PREFACE TO THE SECOND EDITION

The importance of physical chemical generalizations in connection even with the most elementary teaching of chemistry is now generally recognized. That there is a rapidly growing demand for text-books written from this standpoint has been made evident to the author by the large number of letters received from teachers of chemistry in America and Europe, and by the fact that the first edition of this book has been exhausted in considerably less than a year. A number of minor errors have been corrected in the second edition, and the writer will deem it a favor if those who use the book in the future will forward to him any suggestions which might make this work more useful to those for whom it was written.

H. C. J.

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ELEMENTS OF INORGANIC CHEMISTRY

CHAPTER I

THE SCIENCE OF CHEMISTRY

Chemistry a Branch of Natural Science. — The study of nature is ever attracting more and more attention. We are brought in daily contact with the world in which we live, and the mind observes the processes which are going on around it. These are very complex.

If we turn to inanimate nature, we see the rocks crumbling into dust, and furnishing the material of which the soil is made. This is partly dissolved by the waters, or carried mechanically from regions of higher to those of lower level.

If we turn to living matter, the transformations that are taking place are extremely complicated. The seed germinates, takes root, and grows at the expense of the soil, water, and air. The plant is consumed by the animal, which likewise increases in size. The animal dies, decays, and the matter of which it was composed is given back again to the soil, the water, and the air.

The study of nature, or natural science, is so comprehensive and complex that it has been found necessary to divide it into several branches. This is especially true since the mind is not content with simply observing what is transpiring before it, but places matter under new conditions which it can control — experiments with it — and observes the results. The science of chemistry is one of the branches of natural science.

The Kind of Phenomena with which Chemistry is concerned. — While it is impossible at the outset to give any comprehensive

conception of the science of chemistry, certain characteristics of chemical action can be pointed out.

If we connect a piece of copper with an electric battery, an electric current will flow through it. The copper while carrying the current has properties which are different from copper through which no electricity is passing. Disconnect the copper from the electric battery, and it possesses its original properties.

Heat a piece of copper gently, and some of its properties are changed. It will give out heat to surrounding objects; it will occupy a larger volume when hot than at ordinary temperatures. Allow the copper which has been warmed to cool, and it will possess again its original properties; hammer the copper or bend it, and it still remains copper. Changes of this kind are known as physical.

If, on the other hand, we heat a piece of copper to redness in the presence of the air, a far more fundamental change takes place. The copper disappears, and a black substance is formed which has properties quite different from the original copper. The black substance does not look like a metal. It cannot be drawn out into wire. It weighs considerably more than the original copper, and in general has properties sufficiently different from the original copper to show that we are dealing with an entirely different substance. If the black powder is now cooled to the original temperature of the copper, it retains its own characteristic properties.

The change effected in the latter case is, then, far more fundamental than in the former. While certain properties of the copper were changed by passing an electric current through it, or by gently warming it, these properties were restored again when the current was interrupted, or when the temperature was allowed to fall. The original copper remained copper. In the latter case, however, the *composition of the substance was changed*, and this is characteristic of chemical activity. The substances which react chemically lose many of their characteristic properties, and give rise to new substances with very different properties.

Elements and Compounds. — If we look about us, we recog-ize that nature is made up apparently of a great many sub-tances. The soil and the rocks differ greatly in composition n different localities, and are always more or less complex. Vater exists everywhere, and the air is a mixture of many ubstances. When we turn to living matter, we find the com-lexity greatly increased. The simplest living being is com-osed of very complex substances, and the more highly developed rganisms contain a countless number of substances.

This is the way the problem of the composition of the exter-al world, as recognized by our senses, presents itself at first. , however, becomes greatly simplified when we study the com-osition of things in a systematic and comprehensive manner. ll known substances fall into two great classes, — those that nnot be decomposed into simpler substances, and those that n. Take the piece of copper already referred to. By no rocess known to man can it be decomposed into anything mpler than copper.

On the other hand, take the well-known substance water, add little acid to it to make it conduct, and pass an electric cur-nt through it. The water will be decomposed into two simpler bstances, both of them gases, and they will be set free the e at the one pole, the other at the other.

There is, therefore, a fundamental difference between copper d water — the one cannot be decomposed into simpler sub-ances, the other can be decomposed into two substances, both which differ fundamentally in their properties from the sub-ance water.

Substances like copper which cannot be decomposed into ything simpler are known as *elements*, while those substances hich can be decomposed into simpler things are known as *mpounds*.

The Number of Elements and Compounds. — While the chemi-l compounds already known number more than a hundred ousand, the number of chemical elements which have thus r been discovered is only about seventy-five. When we con-

sider that a compound is made up of two or more of these elementary substances, the whole problem of the composition of substances is vastly simplified. We can, then, refer every compound known, both in inanimate nature and in the realm of living matter, to a comparatively few elementary substances.

Take the rocks that are most familiar on the surface of the earth; they are made up chiefly of not more than a dozen elementary substances.

Water, which covers such a large portion of the surface of the earth, is, as we have seen, made up of two elements.

The atmosphere which is so essential to life is made up chiefly of two elements.

If we turn to living matter, we find a very large number of chemical compounds, and the greatest complexity represented. Cellulose, starch, albumen, are among the most complex substances known to the chemist; yet, an analysis of these substances brings out the surprising fact that they contain scarcely more than a half-dozen elements.

The number of chemical elements known to us at present is, as already stated, about seventy-five.

The Chemical Elements. — Having learned what is meant by the term "chemical element," we naturally ask which are the elements and what substances are compounds? In the following table the substances which have been shown with a reasonable degree of probability to be elementary, are given, together with the symbol which is used for the element in question. The elements in **heavy type** are either the most abundant in nature, or the most important chemically. Those in *italics* are next in order of importance, while those printed in ordinary type are either rare in nature or are chemically of subordinate importance.

Aluminium	Al	Bismuth	Bi
Antimony	Sb	*Boron*	B
Argon	A	*Bromine*	Br
Arsenic	As	*Cadmium*	Cd
Barium	Ba	Cæsium	Cs

Calcium	Ca	Osmium	Os
Carbon	C	**Oxygen**	O
Cerium	Ce	Palladium	Pd
Chlorine	Cl	**Phosphorus**	P
Chromium	Cr	*Platinum*	Pt
Cobalt	Co	**Potassium**	K
Columbium	Cb	Praseodymium	Pr
Copper	Cu	Rhodium	Rh
Erbium (?)	E	Rubidium	Rb
Fluorine	F	Ruthenium	Ru
Gadolinium	G	Samarium	Sm
Gallium	Ga	Scandium	Sc
Germanium	Ge	Selenium	Se
Glucinum	Gl	**Silicon**	Si
Gold	Au	*Silver*	Ag
Helium	He	**Sodium**	Na
Hydrogen	H	*Strontium*	Sr
Indium	In	**Sulphur**	S
Iodine	I	Tantalum	Ta
Iridium	Ir	Tellurium	Te
Iron	Fe	Thallium	Tl
Krypton	Kr	Thorium	Th
Lanthanum	La	Thulium	Tu
Lead	Pb	*Tin*	Sn
Lithium	Li	*Titanium*	Ti
Magnesium	Mg	Tungsten	W
Manganese	Mn	*Uranium*	U
Mercury	Hg	Vanadium	V
Molybdenum	Mo	Xenon	X
Neodymium	Nd	Ytterbium	Yb
Neon	Ne	Yttrium	Y
Nickel	Ni	*Zinc*	Zn
Nitrogen	N	Zirconium	Zr

The symbol of the element is usually the first letter, or this combined with some other distinctive letter when several ele-

ments begin with the same letter. In some cases, however, the symbol is not taken from the English name of the element, but from the Latin. Thus, the symbol for copper is Cu, from the Latin *cuprum ;* the symbol for iron Fe, from the Latin *ferrum ;* etc.

Some elements occur in very large quantities in the earth, while others are comparatively rare. The following estimate of the composition of that part of the earth which is accessible to us seems on the whole the most reliable: —

Oxygen, percentage in the earth	50.0
Silicon, " " " "	25.0
Aluminium, " " " "	7.2
Iron, " " " "	5.0
Calcium, " " " "	3.5
Magnesium, " " " "	2.5
Sodium, " " " "	2.3
Potassium, " " " "	2.2
Hydrogen, " " " "	1.0
Titanium, " " " "	0.3
Carbon, " " " "	0.2

The earth is thus made up chiefly of nine elements, the remainder occurring in comparatively small quantities.

Chemical Combination. — Certain elements can combine with certain other elements and form compounds. Two elements may combine and form a compound, or three, four, or more elements may combine.

While elementary substances may combine with one another and form compounds, it is not true that any element can combine with any other element. We shall learn that elements with widely different properties generally combine most readily.

The science of chemistry consists, in part, of a study of the elements and the compounds which these elements can form with one another. Certain generalizations have been reached to which chemical reactions between substances conform. Some of these will be considered in the proper places.

CHAPTER II

OXYGEN

Occurrence in Nature. — Oxygen is the most abundant of all the chemical elements. It forms 88.8 per cent of all the water on the earth, and about 23 per cent of the atmospheric air. It is an important constituent of most of the rocks, and occurs in nearly all living matter whether vegetable or animal. It is estimated in general that about one-half of the earth's crust is composed of the element oxygen.

Preparation of Oxygen. — Since oxygen occurs in such large quantities in nature, we would think that we should turn to some natural source for a supply of this element. It is, however, not very easy to obtain pure oxygen from any natural source. One of the most convenient means of obtaining oxygen in the laboratory is by *heating potassium chlorate.* This compound contains about 39 per cent of oxygen, and gives up all of its oxygen when moderately heated.

Another method by which oxygen can be obtained is to *heat manganese dioxide,* a compound of manganese and oxygen which is rich in oxygen. When this compound is heated to a high temperature it gives up a part of its oxygen.

A better method for preparing oxygen is by *heating a mixture of potassium chlorate and manganese dioxide.* Oxygen is evolved in large quantity at a comparatively low temperature, and, on the whole, this is the best method for preparing oxygen in the laboratory.

Oxygen can also be prepared by *heating a compound of mercury and oxygen known as mercuric oxide.* This compound is decomposed by heat into its two elements, oxygen and mercury.

Oxygen can be obtained at ordinary temperatures by *bringing the compound of oxygen and hydrogen known as hydrogen dioxide in contact with manganese dioxide or lead dioxide in the presence of an acid.* Under these conditions one-half of the oxygen liberated comes from the hydrogen dioxide, and the other half from the manganese dioxide or the lead dioxide. This differs from the preceding methods in that the oxygen is obtained at ordinary temperatures.

Substances burn readily in Oxygen. — One of the most characteristic of the chemical properties of oxygen is the readiness with which substances burn in it. Substances which burn comparatively slowly, or will not burn at all in the air, often burn with the greatest readiness in oxygen gas, emitting very bright light and evolving large quantities of heat.

When a splinter of wood which has been burned in part to a coal, and is still glowing, is plunged into a vessel filled with oxygen gas, it bursts again into flame.

When sulphur is ignited in the air, it burns quietly with a pale blue flame. When the burning sulphur is plunged into a vessel filled with oxygen, it bursts into violent combustion, evolving large amounts of heat and light.

A steel watch-spring, or picture wire, dipped into molten sulphur and ignited, will not continue to burn in the air. If after the sulphur is ignited the steel watch-spring is plunged into oxygen gas, the iron will burn with an intense white light, and a large number of highly heated particles will fly off from the iron, producing quite a pyrotechnic effect.

While phosphorus burns quietly in the air, in pure oxygen it burns with great violence. This will be seen to be the case if a piece of ignited phosphorus is plunged into a vessel filled with pure oxygen.

Explanation of the Above Results. — The above results show beyond question that substances which burn slowly in the air, or do not burn at all, burn readily in pure oxygen. This naturally raises the question why is this the case? The air, as we shall learn, is essentially oxygen diluted with about four times

its volume of nitrogen. The number of oxygen particles in a given volume of air is, therefore, much less than in a given volume of pure oxygen. The nitrogen serves to dilute the oxygen. When combustion takes place in pure oxygen, the heat that is liberated is expended in raising the temperature of the oxygen alone, and the rapidity of the combustion depends chiefly upon the temperature of the oxygen gas.

When the oxygen is diluted with an inert gas like nitrogen, much of the heat that is set free during the combustion is expended in raising the temperature of the nitrogen which takes no part in the combustion, and as far as accelerating the combustion is concerned is, therefore, lost.

COMBUSTION

The subject of combustion, or burning, is one that has attracted the attention of chemists from very early times. This would be expected, since combustion is among the most familiar of chemical phenomena.

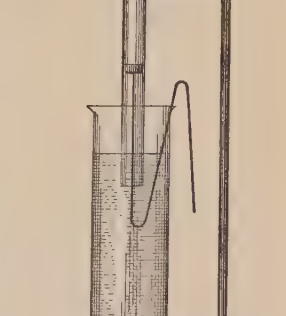

FIG. 1.

Oxygen used up in Combustion. — That oxygen is actually used up in combustion can be readily shown as follows: Fill a glass tube with air and introduce a piece of phosphorus into the tube as shown in Figure 1. The phosphorus will undergo slow combustion, and that the oxygen is being used up is shown by the fact that after a slight expansion due to heating has occurred, the water will rise slowly but steadily in the tube. About one-fifth of the air is thus consumed.

Increase in Weight in Combustion. — If combustion consists in the union of oxygen with the substance burned, then the

weight of the products of combustion must be greater than the weight of the substance that has been burned.

That the products of combustion weigh more than the substance before it was burned can be readily shown by the following experiment. Two pieces of candle of equal length are placed, one upon each pan of a large balance. A lamp chimney is suspended from each end of the arm of the balance. A piece of wire gauze which fits the chimney tightly is introduced into each chimney, and some coarse pieces of caustic soda added. Caustic soda is now added to the lighter side until the pointer stands exactly in the middle of the scale.

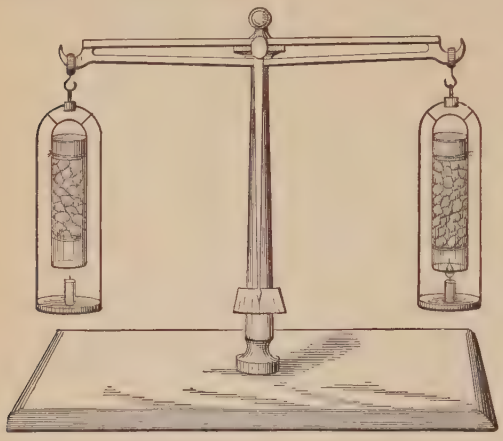

FIG. 2.

One of the candles is now lighted and the products of combustion, carbon dioxide and water, are caught by the caustic soda. After the candle has burned for a time this arm of the balance will begin to sink, showing that the products of combustion of the candle are heavier than the unburned candle.

Combustion consists in the union of oxygen with the substance burned. We have just seen that oxygen is used up in combustion. Also that the weight of the products of combustion is greater than the weight of the substance before it was burned. If we should weigh accurately the substance before it was burned, and the amount of oxygen used up in the combustion, we would find that the sum of these two weights was always exactly equal to the weight of the products of the combustion. This shows that combustion consists in the union of

the substance burned with oxygen, and combustion is nothing but oxidation.

Rapid and Slow Oxidation. — Combustion, as we ordinarily observe it, is a comparatively rapid process. The substance burns up, as we say, in a few minutes, and there is usually a large evolution of heat, and in many cases a marked production of light. This is known as rapid oxidation.

We know oxidation processes, however, which take place slowly and extend over long periods of time, even years. Examples are the oxidation of metals, the decaying or slow oxidation of wood, and the like.

When the oxidation proceeds slowly, as in these cases, there is no apparent evolution of heat and no evolution of light. The question arises, Are we justified in concluding that there is actually no evolution of heat when slow oxidation takes place? We cannot detect any heat set free, yet it might be that there is a slow evolution of heat, but so slow that it escapes before it can be detected.

While we cannot prove directly, unless large masses of substances are employed, that heat is set free in slow oxidation, it can be proved indirectly by methods which it would lead us too far at present to discuss in detail. *Exactly the same amount of heat is evolved* when a given amount of substance is oxidized, whether the combustion takes place slowly or rapidly.

Measurement of the Heat of Combustion. — To measure the amount of heat set free in any chemical reaction, such as combustion, the reaction must be carried out in a vessel surrounded by a poor conductor of heat, so that the loss in heat will be reduced to a minimum. The heat that is produced is allowed to warm a known weight of water, and the temperature of the water is noted before and after the experiment. The apparatus which is used for measuring quantity of heat is known as a *calorimeter*.

Some unit must be adopted for expressing the results of calorimetric measurements. Whatever unit we select would be purely arbitrary. The amount of heat required to raise one

gram of water from 0° to 1° C. is frequently taken as the unit, and is called the *calorie* and written *cal.*

Heat of Formation and of Decomposition. — We have just seen that when two or more substances unite and form a third substance, heat is evolved. Further, a definite amount of heat is set free when a given amount of any substance is formed. This amount is known as the *heat of formation* of the substance.

Given a substance already formed by the union of two or more substances. A certain amount of heat must be added to it to decompose it into its elements. This is known as the *heat of decomposition* of the substance.

A very beautiful relation has been established between the heat of formation of a substance and its heat of decomposition. *The two are equal.*

Certain Physical Properties of the Element Oxygen. — Oxygen under ordinary conditions is a transparent, colorless, odorless gas. It is slightly heavier than air.

One litre of oxygen at zero degrees and under what we call normal barometric pressure, *i.e.* 760 mm. of mercury, weighs 1.4296 grams. Oxygen is only slightly soluble in water, and can, therefore, be collected in vessels over water.

The Pressure of Oxygen varies with the Conditions. — We have referred to the weight of a litre of oxygen under normal conditions of temperature and pressure. This would imply that the weight of a litre of oxygen would change if we changed temperature or pressure, and such is the fact. If we have a litre of oxygen at any given pressure and subject the gas to a greater pressure, the volume would be less than a litre, and, consequently, the density of the gas would be increased and the weight of a given volume of the gas increased. Similarly, diminution in pressure would cause increase in volume and, consequently, diminution in the weight of a given volume of the gas.

If instead of varying the pressure we vary the temperature to which the oxygen gas is subjected, we would also produce change in volume. If the temperature of the gas is increased

and the pressure kept constant, the volume of the gas would increase. If, on the other hand, the temperature of the gas is lowered, the pressure being kept constant, the volume of the gas would be diminished. Certain relations between the pressure and volume, and the temperature and volume of not only oxygen gas, but of gases in general, have been established, but these will be considered later.

The Liquefaction of Oxygen. — Although oxygen is a gas under atmospheric pressure and at all ordinary temperatures, it does not follow that it is a gas at all temperatures and pressures. If we look into the history of the liquefaction of gases, we find, however, that oxygen resisted for a long time all efforts to liquefy it, and was placed among the so-called permanent gases.

It is now readily liquefied and in comparatively large quantity. When oxygen gas is cooled below a certain temperature (— 119°), and then subjected to high pressure, it passes into a liquid. The actual method of liquefying oxygen is, however, more complicated. Liquid oxygen is light blue in color, and boils at — 181° C. under the pressure of the atmosphere. It is a general rule that liquids boil under diminished pressure at a lower temperature than under normal atmospheric pressure. By placing liquid oxygen under greatly diminished pressure a temperature as low as — 225° can be obtained.

EXPERIMENTS WITH OXYGEN

Experiment 1. Preparation of Oxygen from Potassium Chlorate. — (Glass retort holding 100 or 150 cc.; rubber tube; glass tube; pneumatic trough; glass cylinders; potassium chlorate.) Into a small retort *R* (Fig. 3) introduce about 3 grams of potassium chlorate. Connect the retort by means of a rubber tube, with a glass tube *A*, bent as shown in the figure. The trough *T* is filled with water until the end of the tube *A* is covered with water. Heat the retort containing the potassium chlorate gently by means of a bunsen burner *B*. The potassium chlorate at first melts, and then at a somewhat higher temperature a gas begins to escape. After enough gas has been generated to expel the air from the retort and tube, bring the

glass cylinder *C*, filled with water, over the end of the tube *A*, as shown in the figure. When a considerable amount of gas has been liberated, the contents of the retort will become solid, and the escape of gas from the tube *A* will practically cease. If now the temperature is raised considerably higher, oxygen will again be given off and in much larger quantity than in the first stage of the reaction. After a time oxygen will cease to be given off, and no matter how high the temperature is raised, it is impossible to obtain any more oxygen from the solid which remains in the retort. The residue is potassium

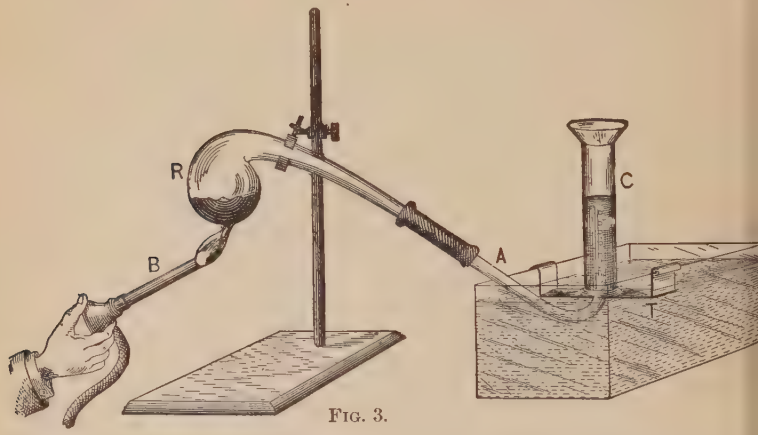

FIG. 3.

chloride, a compound containing only potassium and chlorine, and no oxygen. Prove that the gas is oxygen by means of a glowing splinter. This is obtained by igniting a splinter in a bunsen burner until the end is burned to a coal. Then extinguish the flame and plunge the splinter quickly into the vessel containing the oxygen gas. The splinter will be rekindled into flame by the gas. (See page 7.)

Experiment 2. Preparation of Oxygen from Manganese Dioxide. — (Hard-glass tube closed at one end; manganese dioxide.)

Introduce a few grams of manganese dioxide into a hard-glass tube closed at one end. Heat to a high temperature in a bunsen burner, and show that oxygen is escaping by inserting into the mouth of the tube an ignited splinter from which the flame has been extinguished. It will glow brightly in the oxygen which escapes from the tube. (See page 7.)

Experiment 3. Preparation of Oxygen from a Mixture of Potassium Chlorate and Manganese Dioxide. — (Glass retort holding 200 to 250 cc.; rubber tube; glass tube; pneumatic trough; cylinders; wide-mouthed bottles; bell-jars; etc., manganese dioxide; potassium chlorate.)

Mix 25 grams of manganese dioxide with 25 grams of coarsely pulverized potassium chlorate. Heat a little of the mixture in a test-tube to see that there is no explosion. If the manganese dioxide contains any organic matter mixed with it, as not infrequently happens, an explosion may result when the mixture is heated. If the oxygen is evolved quietly from the mixture when the sample is heated and there is no sign of an explosion, the mixture is introduced into the retort. The apparatus is arranged as in Figure 3. The retort is gently heated, when oxygen will begin to escape. Allow sufficient oxygen to escape to drive the air out of the apparatus; then fill a number of cylinders, bell-jars, bottles, etc., with the gas. It is also convenient to fill some form of large gasometer with oxygen for future use. When all the oxygen which is desired has been obtained, the tube is removed from the trough to prevent the entrance of the water into the retort when the apparatus is allowed to cool. The flame is then removed from the retort, when the evolution of oxygen quickly ceases. (See page 7.)

Experiment 4. Preparation of Oxygen from Mercuric Oxide. — (Glass tube closed at one end; rubber stopper; small glass tube; pneumatic trough; glass cylinder; mercuric oxide.)

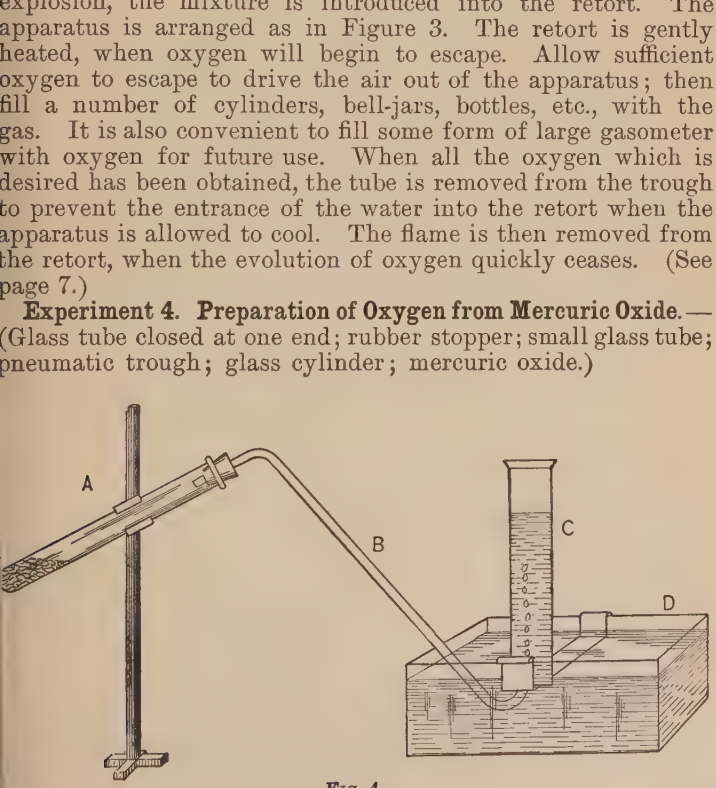

FIG. 4.

Introduce a few grams of mercuric oxide into the glass tube *A* (Fig. 4). This tube is connected with the cylinder *C* by means of the glass tube *B*. The cylinder is filled with water and inverted in the pneumatic trough *D*, also containing water. When the oxide is heated by means of a bunsen burner, oxygen is set free and collects in the cylinder, while mercury condenses upon the colder portions of the tube *A*. Introduce an ignited splinter into the cylinder. The splinter will be quickly rekindled into flame by the oxygen gas. (See page 7.)

Experiment 5. Preparation of Oxygen from a Mixture of Manganese or Lead Dioxide, and Hydrogen Dioxide. — (Test-tube; manganese or lead dioxide; hydrogen dioxide; dilute sulphuric acid.)

Introduce a few grams of manganese dioxide into a test-tube, and a few cubic centimetres of hydrogen dioxide and dilute sulphuric acid. A copious evolution of oxygen will take place. This can be collected in a cylinder as in Experiment 4, or its presence demonstrated by means of an ignited taper. (See page 8.)

Experiment 6. Combustion of Carbon in Oxygen. — (A cylinder filled with oxygen; a piece of charcoal; preferably a porous variety.)

That carbon will burn in oxygen more readily than in the air has already been seen by plunging a splinter from which the flame has been extinguished into a vessel containing oxygen gas. A piece of carbon wrapped with copper wire, which serves to hold it, is heated in a bunsen burner to redness, and quickly plunged into the vessel containing oxygen. It glows brightly in the oxygen, showing far more vigorous combustion than in the air. (See page 8.)

Experiment 7. Combustion of Sulphur in Oxygen. — (A deflagrating spoon; a wide-mouthed bottle or bell-jar holding 2 or 3 litres of oxygen; a piece of sulphur.)

Ignite the sulphur in a deflagrating spoon, and observe that it burns quietly in the air with a pale blue flame. Plunge the burning sulphur into the vessel containing oxygen. The sulphur burns in the oxygen far more vigorously than in the air. This is shown by the character of the flame, which is now completely changed both in magnitude and color. Instead of the small, pale blue flame, which was produced when the sulphur was burned in the air, we have a large, very bright flame with more or less scintillation. Open the vessel and carefully smell the contents. It has the odor of a burning

sulphur match, and thus differs from the original oxygen. (See page 8.)

Experiment 8. Combustion of Iron in Oxygen. — (Steel watch-spring, or picture wire; cotton thread; vessel holding 3 or 4 litres of oxygen; sulphur.)

Wind the lower end of an old steel watch-spring with cotton and dip it into molten sulphur. The sulphur adheres to the cotton in considerable quantity. Ignite the sulphur and plunge the spring into oxygen. The sulphur will burn vigorously and heat the steel to the temperature at which it will begin to unite with oxygen. The iron will then continue to burn in the oxygen, emitting an intense light, and white-hot particles of iron will fly off in all directions (Fig. 5). If a closed vessel is used to contain the oxygen in this experiment, it is advisable to cover the bottom with water, in order that the hot particles of iron falling upon it may not crack the vessel. (See page 8.)

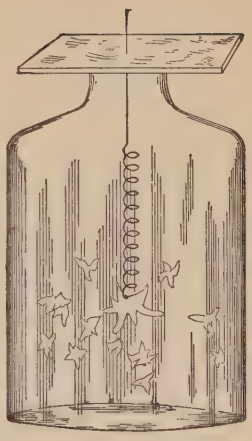

FIG. 5.

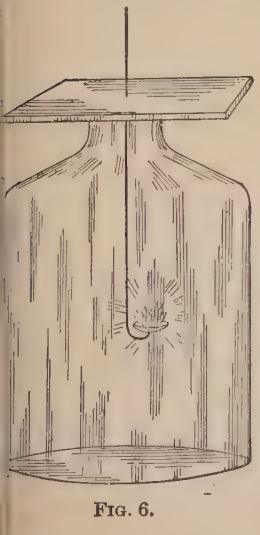

FIG. 6.

Experiment 9. Combustion of Phosphorus in Oxygen. — (A wide-mouthed vessel containing several litres of oxygen; a deflagrating spoon; a small piece of phosphorus.)

Introduce a very small piece of phosphorus (3 or 4 mm. in diameter) into a deflagrating spoon, ignite and introduce into the oxygen. The phosphorus will burn with intense light and heat (Fig. 6). It is well to wrap the vessel containing the oxygen with a towel, so that in case it should break pieces of glass will be prevented from flying. In this experiment the precaution should be taken to cut the phosphorus under water and dry it between pieces of filter-paper. Phosphorus should never be allowed to come in contact with the hand, since bad wounds easily

result. In the above experiment special precaution should be taken to use only a very small piece of phosphorus. (See page 8.)

Experiment 10. Oxygen is used up in Combustion. — (A tall, slender, bell-jar; a deflagrating spoon; sulphur; steel watch-spring.)

This experiment can be performed essentially as Experiments 7, 8, and 9; the difference being that the deflagrating spoon or the watch-spring must fit tightly in a rubber stopper, which is of such size as to close air-tight the neck of the bell-jar containing the oxygen. The bell-jar rests in a vessel holding a considerable amount of water. After the sulphur or iron is ignited the stopper is forced tightly into the neck of the bell-jar. As the sulphur or iron burns the water rises in the bell-jar, showing that the oxygen is being used up in the combustion. (See page 9.)

CHAPTER III

HYDROGEN

Occurrence. — Hydrogen is apparently the most widely distributed of all the elements. It occurs in the sun, especially in the prominences seen during solar eclipses, in the stars, and even in the nebulous masses scattered throughout the universe.

The greatest amount of hydrogen on the earth, by far, is in water, whence the name (*hydro*, water, and *gennao*, to produce). All water contains about 11.2 per cent of hydrogen, and when we consider the amount of water upon the earth, we get some idea of the amount of hydrogen present on our globe. It also occurs in most forms of living matter.

Preparation of the Element Hydrogen. — To obtain the element hydrogen, we would naturally turn to water as the largest source. Hydrogen can be obtained from water by several means. When a little acid is added to water and the electric current passed through the acidified water, hydrogen gas is liberated at one of the poles, and can be easily collected.

Hydrogen can also be obtained from water by purely chemical means. When metallic sodium is brought in contact with water at ordinary temperatures, a violent reaction takes place, and the hydrogen set free is ignited. When potassium is used instead of sodium, a still more violent reaction takes place, and the hydrogen set free is ignited.

In practice we seldom use any of the above methods, since we have means of preparing hydrogen on a large scale which are far more convenient than any of the above. When zinc is treated with a strong acid, such as hydrochloric or sulphuric, the metal passes into solution and the hydrogen from the acid escapes.

Hydrogen is readily prepared as follows: Some pieces of zinc are introduced into a glass flask *A*, as shown in the figure (Fig. 7), and dilute hydrochloric acid poured into the flask through the funnel-tube *B*, until the end of the tube dips beneath the acid. Hydrogen gas will be liberated and escape through the side tube *C*.

If it is desired to prepare hydrogen on a still larger scale, a form of apparatus devised by Kipp (Fig. 8) is very convenient.

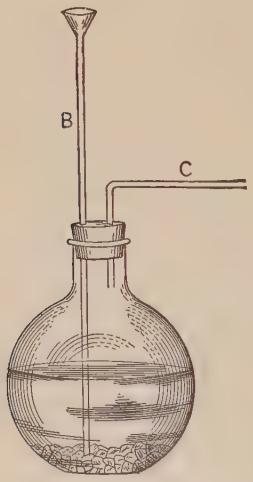

FIG. 7.

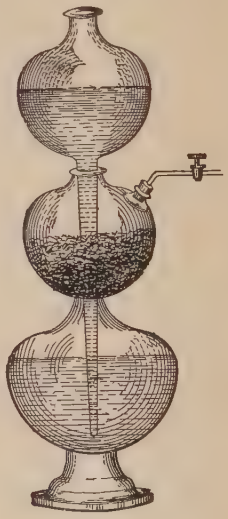

FIG. 8.

From this apparatus hydrogen is obtained by simply turning a stop-cock. When no more gas is desired, the stop-cock is closed, and the pressure of the hydrogen generated automatically drives the acid away from the zinc and prevents the further liberation of gas.

Combination of Hydrogen with Oxygen. — Hydrogen, a colorless and odorless gas, combines readily with oxygen at elevated temperatures. A mixture of hydrogen and oxygen can be kept for an indefinite time, provided the mixture is not heated. If

the temperature is raised sufficiently, the two combine with the greatest ease, producing a violent explosion.

That hydrogen can be burned in the presence of oxygen without any explosion taking place can be readily shown. A rubber tube is attached to the end of the small glass tube *C* (Fig. 7), and into the other end of the rubber tube a metallic tube with a very fine opening is inserted. The small tube at the end of a mouth-blowpipe works very well. The hydrogen is allowed to escape from the apparatus through the metallic tube until every trace of air has been removed from the apparatus. The hydrogen is ignited at the end of the metal tube. It will burn with a flame which is nearly colorless, but which is intensely hot, as can be shown by inserting a piece of metal into the flame.

That water is formed in this process can be readily demonstrated as follows: A cold, dry, glass cylinder is brought over the flame of burning hydrogen, and held in position for a few moments. The inner wall of the cylinder will quickly become covered with moisture, and after a short time drops of water will form on the walls of the cylinder and fall from the mouth.

The explosive nature of the mixture of hydrogen and oxygen can be readily demonstrated by the following experiment: Two volumes of hydrogen gas are mixed with one volume of oxygen gas, and some of the mixture conducted through a solution of soap until a mass of soap bubbles has been formed. The solution of soap should be placed in a thick-walled, porcelain evaporating dish. The dish containing the soap bubbles is set in a protected place such as under the hood, and the flame of a gas-lighter brought carefully up to the bubbles filled with the mixture of hydrogen and oxygen. An explosion whose violence depends on the size and number of the bubbles present will take place. It is well, therefore, not to have any great amount of the mixed gases present when the flame is applied.

This mixture of the two gases containing two volumes of hydrogen to one of oxygen is known as *detonating gas* or

electrolytic gas, since it is the same mixture which is obtained when an electric current is passed through acidulated water and the gases liberated at the two poles allowed to mix.

Relations by Volume in which Hydrogen and Oxygen Combine. — It was discovered early in the nineteenth century that hydrogen and oxygen combine in simple volume relations. No matter in what proportions the gases hydrogen and oxygen are mixed, for every volume of oxygen that disappears when combination takes place two volumes of hydrogen disappear. The ratio of the volumes which combine is, therefore, one to two.

The further question that remains is what relation exists between the volumes of the gases which combine and the volume of the water-vapor formed?

Two volumes of hydrogen gas combine with one volume of oxygen gas and form two volumes of water-vapor. Three volumes of the constituent gases have disappeared, and two volumes of the product have been formed. There has been a contraction in volume of one-third.

We shall learn from a study of other cases that this is a general relation. *Gases combine in simple volume relations, and there is a simple relation between the volumes of the gases which enter into combination and the volume of the product formed.*

Heat Energy produced when Oxygen and Hydrogen Combine. — That there is a large amount of heat energy produced when oxygen combines with hydrogen is shown by the fact that the vessel which contains the gases becomes appreciably heated. It has been utilized as a source of very high temperature in a form of lamp which we shall now describe.

The Oxyhydrogen Blowpipe. — The oxyhydrogen blowpipe is a form of apparatus in which hydrogen is so burned in oxygen as to concentrate the heat in a small space. The apparatus is represented in Figure 9. The hydrogen enters through the side-tube *H*, and is lit at *E*. Oxygen enters through the tube *O* and does not mix with the hydrogen until the flame is reached.

The flame of the oxyhydrogen blowpipe gives very little light, but is intensely hot. It will give some idea of the temperature of the flame to state that platinum can be easily melted in it.

While the flame of the oxyhydrogen blowpipe is itself only slightly luminous, an intense light can be produced by allowing it to fall upon certain substances which can be heated to a high temperature without fusion. Such a substance is ordinary lime. When the oxyhydrogen flame is allowed to fall upon a cylinder of lime, an intense white light is produced.

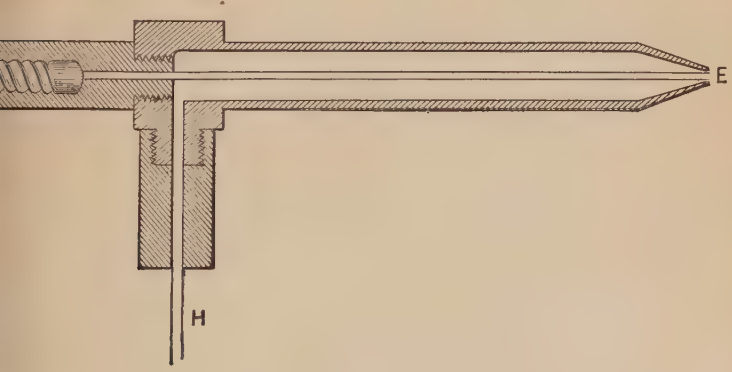

FIG. 9.

This is the *Drummond light.* The light is so intense that it can be used where high illumination is required, as in projecting lanterns and the like.

The Reducing Power of Hydrogen. — The tendency of hydrogen to combine with oxygen manifests itself, not only when the oxygen is in the free state, but even when it is combined with other elements.

Take the oxide of zinc. When hydrogen is passed over this substance at an elevated temperature, it combines with the oxygen and leaves the zinc reduced to the elementary condition.

The removal of oxygen from a compound is known as *reduc-*

tion, and the substance which can remove the oxygen as a *reducing agent.*

Nascent Hydrogen. — When hydrogen is first liberated by the action of an acid on a metal, it has very different properties from those which it possesses after it has once been formed. While hydrogen gas, as we ordinarily know it, must be heated to an elevated temperature before it will reduce the oxides of most metals, hydrogen which is just being formed will reduce many such substances even at ordinary temperatures. Many other reactions which hydrogen gas will either not effect at all, or effect only at elevated temperatures, will be produced readily at ordinary temperatures by hydrogen which is just being formed.

Hydrogen which is just being formed has acquired a specific name to distinguish it from hydrogen which has been formed for an appreciable time. It is known as *nascent hydrogen.* This condition of the nascent state we shall learn is not peculiar to hydrogen, but is possessed by other elements as well.

Certain Physical Properties of the Element Hydrogen. — Hydrogen is a transparent, colorless gas, without taste or odor. It is the lightest of all known substances, being nearly sixteen times lighter than oxygen. One litre of hydrogen at normal temperature and pressure weighs only 0.08995 gram. The relative lightness or small density of hydrogen can be shown in a number of ways.

If a small balloon or light sack of any kind which will hold a gas is filled with hydrogen, the mouth tied, and the balloon set free, it will rise rapidly in the air, showing that hydrogen is considerably lighter than air. This is made use of on a large scale by aeronauts for ascending to considerable heights in the atmosphere. A large silk balloon is filled with hydrogen, and it will not only rise in the atmosphere but will carry considerable weight with it. When it is desired to descend, the hydrogen is allowed to escape through a valve into the air.

A still more striking illustration of the small density of hydrogen is shown by an experiment based upon the *rate at*

which hydrogen gas diffuses. There is a well-known law connecting the rates at which gases diffuse with their densities.

Gases diffuse with velocities which are inversely proportional to the square roots of their densities.

The lighter the gas, the more rapidly, then, will it diffuse. That hydrogen diffuses rapidly can be shown by the following experiment (Fig. 10): A hollow porous cup *C* is fastened to a glass tube *R*, which extends into the flask *F*, passing through a stopper which tightly closes the mouth of the flask. A second glass tube *T*, drawn out to a fine opening, passes through a second stopper and dips beneath the water in the flask. A large bell-jar *V* is now filled with hydrogen and placed over the porous, porcelain cup. Hydrogen diffuses rapidly in through the cup, due to the small density of the gas, produces a pressure inside the apparatus, and this forces the water up into the glass tube *T*, and out through the small opening. In this way quite a fountain can be produced.

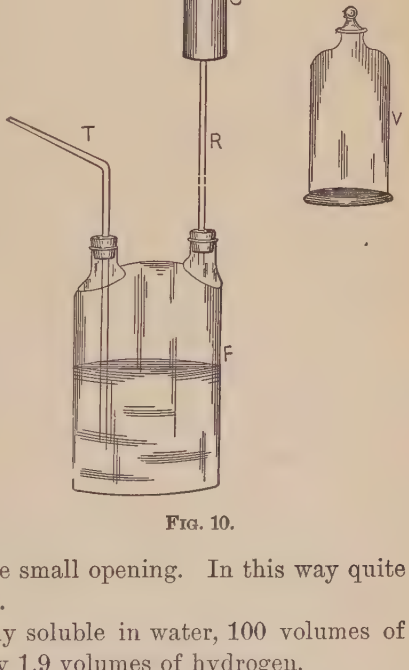

Fig. 10.

Hydrogen is only slightly soluble in water, 100 volumes of water at 15° dissolving only 1.9 volumes of hydrogen.

The Liquefaction of Hydrogen. — Hydrogen like oxygen was one of the few gases which resisted liquefaction until quite recently. When liquid oxygen is allowed to evaporate under low pressure, a temperature of − 210° to − 225° can be produced. If hydrogen under a pressure of several hundred atmos-

pheres is cooled by liquid oxygen to — 200° or — 225° and then is suddenly allowed to expand, it will in expanding cool itself to its point of liquefaction.

The liquefaction of hydrogen in appreciable quantities we owe almost entirely to Dewar. He has shown that its boiling-point is — 252°. It is, however, possible to reach a still lower temperature by a method which has now become familiar to us. By allowing liquid hydrogen to boil under greatly diminished pressure, still further cooling is produced, and a temperature as low as — 258° has been realized. Under these conditions the hydrogen solidified.

Properties of Liquid Hydrogen. — Liquid hydrogen is colorless and transparent, and has small viscosity. The supposed blue color of liquid hydrogen is due to impurities. It has a density of 0.07, water being unity. By contact with liquid hydrogen, oxygen (and as we shall learn also air) is converted first into a liquid and then into a solid, or is frozen, as we say.

A beautiful and thrilling experiment has been performed by Dewar, who has liquefied hydrogen by the litre. Liquid hydrogen was poured into a test-tube and the tube exposed to the air. Liquid air soon began to stream off the test-tube, and finally the tube became covered with frozen air. The remarkable character of this experiment is evident to any one.

EXPERIMENTS WITH HYDROGEN

Experiment 11. Preparation of Hydrogen by the Action of Hydrochloric or Sulphuric Acid on Zinc. — (Glass flask of 400 to 500 cc. capacity; thistle tube; glass tubing; cylinders for collecting gas; granulated zinc; hydrochloric or sulphuric acid.)

Arrange the apparatus as shown in Figure 7. Into the flask *A* introduce some granulated zinc, and through the tube *B* pour hydrochloric acid or sulphuric acid. If hydrochloric acid is used, a dilution of one acid to two water is convenient. The sulphuric acid to be used is prepared by adding concentrated sulphuric acid slowly with constant stirring to six times its volume of water.

If the zinc is fairly impure, as is ordinarily the case, the

rapid evolution of hydrogen begins at once. Allow the hydrogen to escape until *every trace of air has been removed from the apparatus.* Fill a test-tube with the gas and ignite; an explosion shows that the vessel still contains air. This is of fundamental importance, since if there is any oxygen mixed with the hydrogen, dangerous explosions will result in subsequent experiments.

Granulated zinc is used on account of the comparatively large surface exposed to the action of the acid. If purer zinc is employed and the action with acids is slow, add a few drops of platinic chloride to the zinc, when a rapid evolution of hydrogen will take place.

The hydrogen can be readily dried by passing it through a cylinder containing concentrated sulphuric acid. If comparatively pure hydrogen is desired, it can be passed first through a solution of potassium permanganate to which a little sulphuric acid has been added, and then through concentrated sulphuric acid to remove the water.

Fill a number of vessels with hydrogen by displacement of water, as with oxygen. In working with hydrogen the *Kipp apparatus* (Fig. 8) is very convenient. The middle bulb is partly filled with granulated zinc, the lower bulb with dilute sulphuric acid, which extends also into the upper bulb. When the stop-cock is open, the sulphuric acid comes in contact with the zinc and hydrogen is evolved. When the stop-cock is closed, the hydrogen generated forces the sulphuric acid off of the zinc into the lower and upper bulbs, and the generation of hydrogen ceases. When the gas is wanted, it is only necessary to open the stop-cock and obtain any desired quantity. (See page 20.)

Experiment 12. Combustion of Hydrogen. — (Kipp apparatus for generating hydrogen; small tip of a blowpipe; platinum wire.)

Connect a Kipp apparatus for generating hydrogen, or the apparatus described in Experiment 11, with the small tip of a mouth-blowpipe, by means of a rubber tube fastened very tightly to the tip to prevent any air from mixing with the hydrogen. Allow the hydrogen to flow for a time and then ignite the jet. The hydrogen will burn with a nearly colorless flame, which, however, is intensely hot, as can be shown by holding in the flame a piece of platinum wire.

If hydrogen is burned from a glass tube, the flame will be colored yellow, due to the presence of sodium in the glass. (See page 21.)

Experiment 13. Reducing Power of Hydrogen. — (Hard-glass tube closed at both ends by one-hole rubber stoppers; Kipp apparatus for generating hydrogen; glass cylinder; copper oxide; sulphuric acid.)

Arrange the apparatus as shown in Figure 11. The copper oxide is introduced into the glass tube at *C*, and the tube connected with the drying cylinder *T*, which, in turn, is connected with the hydrogen generator by means of a rubber tube. The drying cylinder is partly filled with concentrated sulphuric acid. The hydrogen is admitted through the glass tube *B*. When the hydrogen has been passed through the tube until every trace of air has been removed, the glass tube is heated at *C* by means of a bunsen

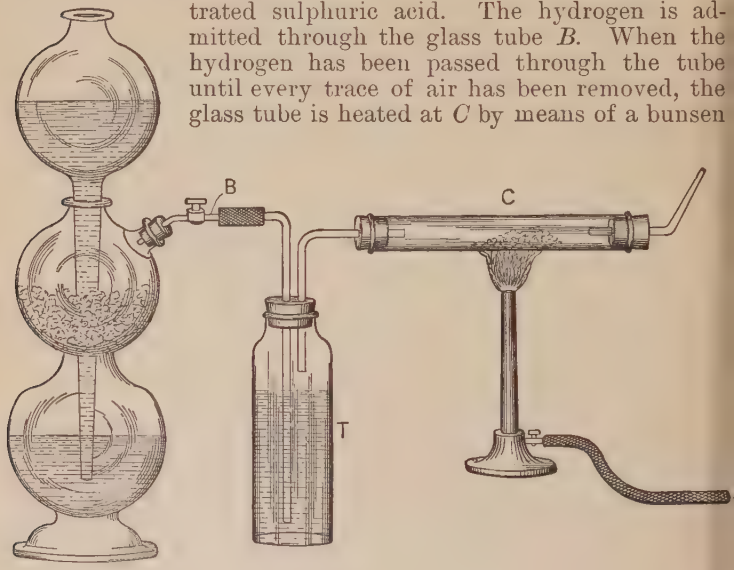

FIG. 11.

burner. The copper oxide is gradually reduced by the hydrogen, yielding red, metallic copper. Water collects in the end of the glass tube beyond the flame. (See page 23.)

Experiment 14. Water formed when Hydrogen is burned in the Air. — (Hydrogen generator; U-tube filled with calcium chloride; bent glass tube; bell-jar ½ litre.)

Arrange the apparatus as shown in Figure 12. The hydrogen is passed through the calcium chloride to remove the moisture, and then ignited at the end of the tip. The bell-jar is placed over the flame so that the flame does not touch the walls. As

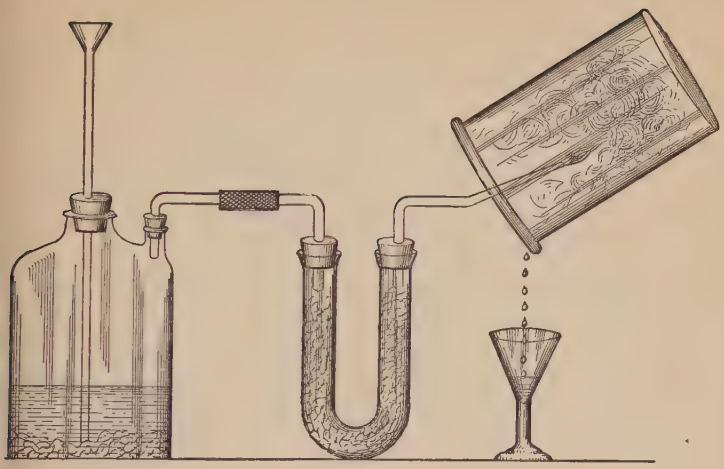

FIG. 12.

the hydrogen burns, water collects upon the walls of the bell-jar, and drops from the lower edge. (See page 21.)

Experiment 15. Hydrogen Lighter than Air. — (Two glass cylinders, holding about 1 litre each.)

Fill one cylinder with hydrogen and cover the mouth with a ground-glass plate. Bring the mouth of this cylinder beneath the mouth of a similar cylinder filled only with air, and placed with its mouth downwards (Fig. 13). Hold the cylinders in this position for a few seconds, and then apply a lighted match to the mouths of the two cylinders. It will be found that the hydrogen has passed from the lower cylinder into the upper, — has been poured upwards, — displacing the air in the upper cylinder. (See page 24.)

Experiment 16. Hydrogen Lighter than Air. — (Chemical balance; large beaker; vessel holding from 2 to 3 litres of hydrogen.)

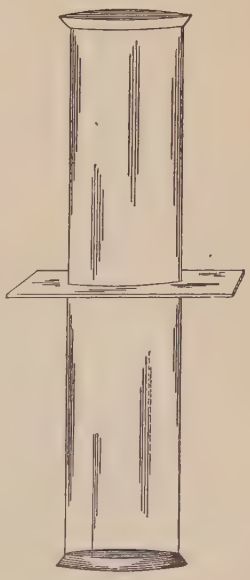

FIG. 13.

Use the same chemical balance as in Figure 2. Remove both lamp chimneys, replacing one by a scale pan, and the other by a large beaker which is suspended from the arm of the balance in an inverted position. Add weights to the scale pan until the pointer stands at zero. Then allow the hydrogen to flow from the containing vessel upwards into the beaker. This arm of the balance will rise, showing that the hydrogen is lighter than the air which it displaced.

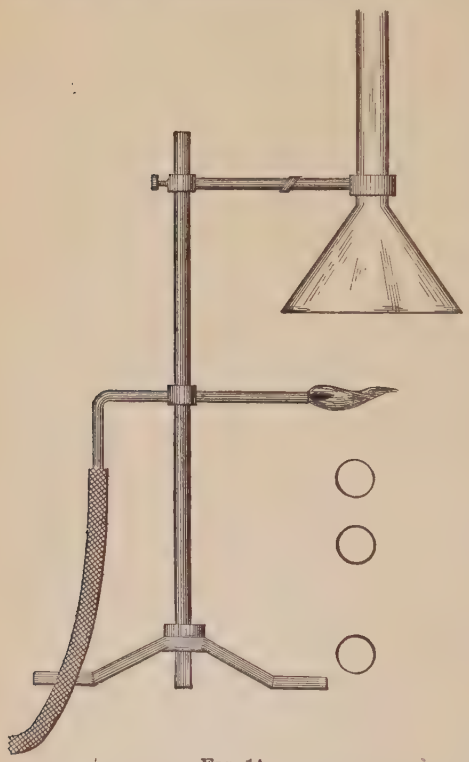

Fig. 14.

This arm will begin to fall again after a short time, due to the rapid rate of diffusion of the hydrogen out into the surrounding air. (See page 24.)

Experiment 17. Hydrogen Soap Bubbles rise in the Air. — (A saturated solution of soap containing about one-half its volume of glycerine; Kipp apparatus for generating hydrogen; a thistle tube or a smoker's pipe.)

The small end of the thistle tube or pipe is introduced into the soap solution, and the excess of liquid shaken off. The hydrogen is carefully admitted from the Kipp apparatus, when the soap bubble filled with hydrogen gas gradually forms. By jarring the tube or pipe the bubble is set free and rises rapidly in the air. By arranging a gas-jet as shown in Figure 14, and inverting a large funnel above it, the hydrogen soap bubble is drawn into the flame and explodes. (See page 24.)

Experiment 18. Diffusion of Hydrogen. — (Unglazed porcelain cup; glass tube; glass bottle; bell-jar filled with hydrogen.) Arrange an apparatus as shown in Figure 10. The tube *R* just passes through the rubber stopper. The tube *T* drawn out to a fine point dips beneath the surface of the liquid. Bring the vessel *V*, filled with hydrogen, over the porous cup. Hydrogen diffuses rapidly through the cup, and produces such a pressure on the water in the vessel that a spray of water is thrown out of the fine opening of the tube *T*. (See page 25.)

CHAPTER IV

WATER

Occurrence of Water. — Water, on account of its very wide distribution over the surface of the earth, is probably the best known chemical compound. In the free condition it covers about three-fourths of the surface of the earth. Further, it is widely distributed through the rocks over the surface of the earth, each cubic metre of rock containing on the average about one litre of water. It exists in large quantities in the atmosphere, in the form of water-vapor. It also exists in combination with a large number of substances as *water of crystallization*, or *water of hydration*. Its presence is not limited to inorganic or inanimate nature. *It forms an essential part of all living matter.* The main constituent of living matter as far as mass is concerned is water. The human body is more than two-thirds water, and the animal and vegetable food which we eat contains scarcely less water in proportion to solid matter.

Water as it occurs in Nature is Impure. — It is safe to say that all natural water contains impurities. This does not refer to impurities which are thrown into water artificially, as by the drainage of human habitations, but to impurities which we may call natural. The water of the sea is very impure because of matter dissolved from the soil and rocks by the waters before they reach the sea, and after they have been poured into it. The waters of small streams and rivers are impure for the same reason. If water has come in contact with soil containing a large amount of limestone, and especially if there is much organic matter in the soil, it will dissolve large quantities of the limestone and is then what we call *hard water*.

If, on the other hand, the water has fallen upon a region which contains mainly sandstone or other difficultly soluble rocks, but little of the solid matter will dissolve, and we have then comparatively pure water. This is the reason why water from mountains composed of granite or sandstone is relatively pure.

Rain-water would undoubtedly be fairly pure were it not contaminated while in the atmosphere. However, while it exists in the atmosphere in the form of vapor it takes up many kinds of impurities, and especially after it is formed into drops and falls through the atmosphere, foreign matter is dissolved by it.

From the above it is then obvious that all natural waters contain impurities, but that the amount of impurity varies greatly from one sample of water to another.

Mineral Waters. — In certain localities minerals exist which are more or less soluble in water. Rain-water or water from other sources dissolves these substances and holds them in solution. Such waters are known in general as *mineral waters*, the nature of the water depending upon the nature of the mineral in solution.

Purification of Water. — Water is usually rendered impure in the way described above, by carrying with it in solution dissolved substances. It may, however, be rendered impure by matter which is not in solution, but simply in a state of *mechanical suspension*. This latter condition is illustrated by small streams after a heavy rain. The finely divided soil is carried along with the water in a state of fine suspension, and we have *muddy water*.

When the impurity is in a state of mechanical suspension and is not in solution, it can be removed by *filtration*. Filtration consists in passing water through a substance with very fine openings or pores, so fine, indeed, that the particles of water can pass, but not the particles held in mechanical suspension. This is effected on a small scale in the laboratory by means of certain varieties of paper known as "*filter-paper*."

If the impurity in the water is in solution, it is obvious that we cannot separate it by any mechanical process such as filtration. Some other principle must be utilized. When water containing non-volatile impurities is boiled, the vapor which escapes is practically pure. If this vapor is condensed again, we have practically pure water. This process of converting a liquid into vapor and recondensing the vapor is known as *distillation*, and the apparatus in which a distillation is carried on as a *still*.

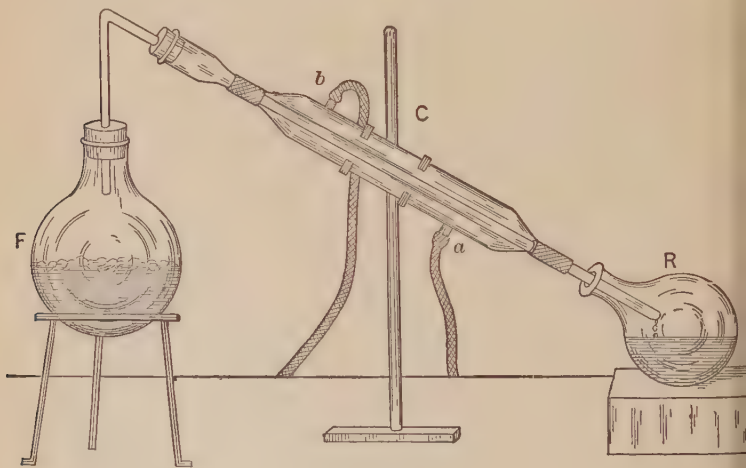

FIG. 15.

The form of still which is used when only a small amount of liquid is to be distilled is shown in Figure 15. Into the glass flask *F* the liquid to be distilled is introduced. This is heated and converted into vapor by a burner placed beneath the flask. *C* is the condenser, consisting of a small inner glass tube surrounded by a much larger glass-jacket. Cold water is passed into the jacket at *a*, and out at *b*. The vapor in the inner tube is condensed to a liquid as it passes through the condenser, and flows into the receiver *R*.

If it is desired to distil a liquid on a large scale, the form of

the apparatus is greatly modified, but the principle is exactly the same as in the apparatus described above.

Water not an Element, but a Compound. — Water is the first substance that we have thus far studied which is not an element, but is composed of more than one element.

That water is not an element is obvious from our studies of oxygen and hydrogen. We have seen that by electrolysis both oxygen and hydrogen can be obtained from water; and an element, by definition, is a substance which cannot be decomposed into any other substances.

Composition of Water. — We have seen that oxygen and hydrogen can be obtained from water, but this does not show that water contains only these two elements. To answer this question two general methods are available. First, decompose water, and see whether anything but hydrogen and oxygen is obtained. Second, cause oxygen and hydrogen to combine, and see whether water is formed.

The most convenient means of decomposing water is the electric current. When a little acid is added to water to diminish its resistance to the flow of the current, and an electric current is passed through it, it is decomposed. This process of effecting decompositions by means of the current is known as *electrolysis*.

Electrolysis of Water. — The only products obtained by the electrolysis of water are the two gases, oxygen and hydrogen; oxygen being set free at the anode and hydrogen at the cathode. That these are oxygen and hydrogen, respectively, can be shown by the fact that the former will ignite a match which has just been extinguished, and the latter will burn with the characteristic hydrogen flame.

If we wish to know the relative volumes of the two gases set free from water, we must collect and measure them.

A convenient form of apparatus for effecting the electrolysis of water and collecting the gases set free is the following: —

Into the two arms A and B (Fig. 16) of the U-tube are inserted two platinum electrodes. These tubes are completely

filled with acidulated water by filling the reservoir *R* to the desired height, and opening the two stop-cocks at the ends of *A* and *B*. The current is passed into the solution through the electrode in *B* and out through the electrode in *A*. The stop-cocks are closed before the current is passed, and oxygen collects in *B*, and hydrogen in *A*. When the current has been flowing for a short time it will be observed that the gas is collecting in *A* faster than in *B*. The tubes *A* and *B* are graduated so that at any moment the amounts of gases set free can be read off at once. After an appreciable amount of gas has collected in *B*, interrupt the current and read the volumes of the gases in the two tubes. It will be found that there is just *twice* the volume of gas in *A* that there is in *B*. Close the circuit, and allow the electric current to flow until a considerably larger volume of the two gases has been set free. Interrupt the current again, and measure the volumes of the two gases. It will be found that the volume of the hydrogen is again *exactly double* that of the oxygen.

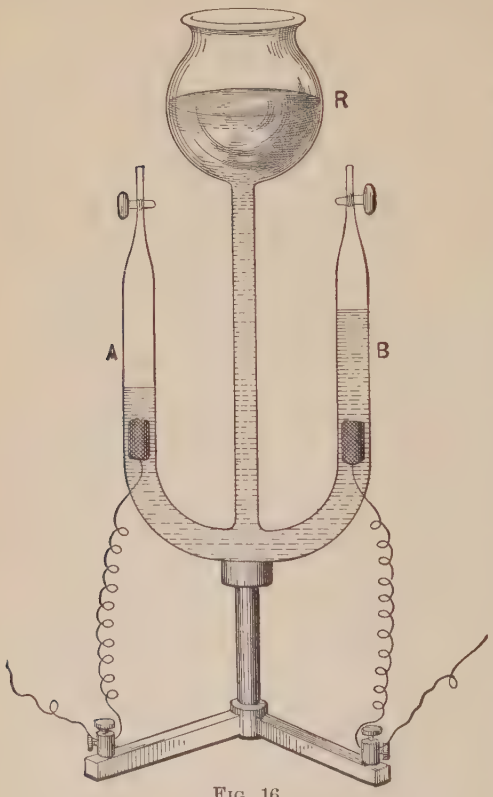

FIG. 16.

No matter how long the current is allowed to flow, nor how much water is decomposed, we would always find that the volume of the hydrogen set free was exactly double that of the oxygen. From the decomposition of water, or by the *analytical method*, we are therefore led to the conclusion that water is made up by the union of two volumes of hydrogen with one volume of oxygen. To determine the composition of water, however, we are not dependent solely upon the analytical method. We can use also the *synthetical*.

Synthesis of Water. — If water is composed of two volumes of hydrogen to one volume of oxygen, then, when we mix two volumes of hydrogen with one volume of oxygen and pass an electric spark through the mixture which causes the gases to combine, all the hydrogen should combine with all the oxygen and form water. This is exactly what takes place. Whenever two volumes of hydrogen are mixed with one volume of oxygen and the gases made to combine by means of an electric spark, or by rise in temperature, all the hydrogen and all the oxygen are used up and water is formed. If more than two volumes of hydrogen are used, all the oxygen will be used up and the excess of hydrogen will remain uncombined. If less than two volumes of hydrogen are used, all the hydrogen will be used up and the excess of oxygen will remain.

The results of synthesis confirm those of analysis; viz. that water is formed by the union of two volumes of hydrogen with one volume of oxygen.

Chemical Behavior of Water. — All things considered, water is probably the most important chemical compound known. It is formed, as we have seen, by the union of hydrogen and oxygen. Few compounds known are more stable than water. If we try to decompose it into its elements, we will appreciate what this means. It is true, as we have seen, that it can be decomposed into its elements by means of the electric current. If we try to decompose water into its elements by heat, enormous temperatures are required. In order to effect even slight decomposition a temperature of 1000° or higher is neces-

sary, and a considerable amount of decomposition is effected only when temperatures between 2000° and 3000° are employed.

Stress is laid upon these facts for the purpose of illustrating a general principle. *When a chemical compound is formed with great evolution of heat, it is almost always a very stable substance.*

Water has the power of combining with a certain class of chemical compounds known as the oxides, converting some of them into the important class of compounds known as the bases, and others into the very important class of compounds known as the acids.

The subject of acids and bases will be considered in detail when the elements which form these substances are studied. Many substances crystallize from solution in water with a large amount of water in their crystals. This is known as *water of crystallization.* This water is frequently driven off completely when the crystals are heated to 100° — the boiling-point of water. In some cases the crystals lose a part of their water even at ordinary temperatures. Such substances are known as *efflorescent.*

Other substances when exposed to the air at ordinary temperatures take up water. Such substances are known as *deliquescent.*

Certain Physical Properties of Water, *Boiling-point.* — Water at ordinary temperatures and pressures is a colorless liquid. In very thick layers it has a bluish tint. Under a pressure of 760 mm. of mercury it boils at 100° C.; *i.e.* at this temperature the tension of the aqueous-vapor is just sufficient to overcome the superincumbent pressure, which is the pressure of the atmosphere. As the pressure to which the water is subjected increases, its boiling-point rises. Under a pressure of five atmospheres the boiling-point of water is 152°. Under a pressure of ten atmospheres water boils at 180°.3, while under a pressure of twenty atmospheres it does not boil until a temperature of 213° is reached.

These are the conditions which obtain in a steam-engine. The water is under the pressure of its own vapor, which amounts to from five to ten or twelve atmospheres, and consequently its boiling-point is very greatly raised.

Similarly, water boils much lower on a high mountain than in a valley. As we ascend a mountain the pressure of the atmosphere becomes less, and, consequently, the pressure which the tension of the water-vapor must overcome. On the top of Mont Blanc water boils at about 84°.

Heat of Vaporization. — Any one who ever observed water boil must have been impressed by the enormous amount of heat which is required to convert the liquid into vapor. He must have been further impressed by the fact that the temperature of the vapor is practically the same as that of the liquid from which it was formed. The amount of heat required to convert one gram of water at 100° into vapor at 100° is 540 calories, *i.e.* the same amount of heat which would be required to raise 540 grams of water 1° in temperature. This is known as the *heat of vaporization of water.*

The Freezing of Water. — When water at ordinary pressure is cooled to 0° it freezes, as we say, or passes into ice. As we cool water down towards its freezing-point, it contracts in volume until a temperature of 4° is reached. As the temperature is further lowered from this point, the water begins to expand and continues to do so until the freezing-point is reached.

The importance of this apparently insignificant fact is very great indeed from the standpoint of the economy of nature. Since water expands from 4° to the freezing-point, ice is lighter than water and floats upon it. The importance of ice floating upon water and not sinking to the bottom is twofold. In the first place, it protects the water from the extreme cold of the atmosphere, since ice is relatively a poor conductor of heat; and in the second place, if ice sank to the bottom of our streams as fast as it was formed, this would continually expose a fresh surface of the water to the cold, and our streams might be frozen solid, which would mean the extermination of all living things within them.

Heat of Fusion of Ice. — We have just learned what an enormous amount of heat energy must be expended to convert water into vapor. We shall now see that a large amount of heat is

required to convert ice into water. The amount of heat required to convert one gram of ice at 0° into water at 0° is 80 calories, *i.e.* the amount of heat which would raise one gram of water from 0° to 80°. This is known as the *heat of fusion of ice.*

Of all well-known liquids water has the highest *specific heat.* By the specific heat of water is meant the amount of heat required to raise a given amount of water, say a gram, one degree in temperature. This amount of heat, as we have seen, is one calorie. One calorie of heat will raise a gram of any other well-known substance more than one degree in temperature. Water thus stands at the head of the list of well-known substances as far as specific heats are concerned.

Similar results would be obtained if we ran through the whole list of properties. Water would stand in practically every case either at the top or bottom of the list of substances. Its properties are, therefore, distinctly extreme. They are either a maximum or a minimum, and usually a maximum.

Solvent Power of Water. — Water has a remarkable power to dissolve other substances which are brought in contact with it. Indeed, of all known substances it is the best solvent, and with respect to this property it also stands at the very head of the list of chemical substances. The importance of solution for chemistry cannot be overestimated. This becomes obvious when we consider that most chemical reactions take place in solution.

Unsaturated and Saturated Solutions. — When water has dissolved a certain amount of a given substance, but is still capable of taking up more of it, the solution is said to be unsaturated. When water has dissolved all of a given substance which, at the temperature in question, it can take into solution, the solution is said to be saturated.

EXPERIMENTS WITH WATER

Experiment 19. Distillation; Separation of Volatile from Non-volatile Substances. — (Flask holding 1 litre; condenser; receiver; ammonia; copper sulphate.)

Arrange an apparatus as in Figure 15. Introduce into the flask *F* water containing a little ammonia. Distil the liquid. Both water and ammonia will pass over, as can be proved by the odor of the distillate and its reaction with red litmus. This is because ammonia is volatile as well as water.

Rinse out the condenser and receiver and add copper sulphate in solution to the flask *F*, until it no longer contains any free ammonia. Now distil the contents of the flask. Pure water will pass over, since neither copper sulphate nor copper hydroxide is volatile.

Repeat the above experiment, adding to the flask *F* water containing a little potassium permanganate. (See page 34.)

Experiment 20. Electrolysis of Water. — (Hofmann electrolytic apparatus.)

The apparatus used is shown in Figure 16. Fill the apparatus with an eight per cent solution of sulphuric acid by pouring the solution into the large bulb *R*, the stop-cocks being open. As quickly as the arms are entirely filled, close the stop-cocks and remove by means of a piece of filter-paper any liquid in the tubes beyond the stop-cocks. Pass an electric current through the solution. The gases will collect over the two electrodes in the two arms of the apparatus. Over one electrode the gas will collect just twice as fast as over the other. After a considerable amount of gas has been collected in each arm, test the smaller volume of gas for oxygen and the larger volume for hydrogen.

This experiment shows that two volumes of hydrogen combine with one volume of oxygen, forming water. (See page 35.)

Experiment 21. Quantitative Synthesis of Water by the Action of Hydrogen on Copper Oxide. — (Same apparatus as in Experiment 13, with the addition of a U-tube.)

Arrange an apparatus as in Figure 17, conducting the hydrogen through a U-tube containing calcium chloride, and a cylinder partly filled with concentrated sulphuric acid. Weigh the amount of copper oxide used, and weigh the mixture of copper and copper oxide after the experiment is completed. Weigh the cylinder containing concentrated sulphuric acid, before the experiment, and weigh the cylinder and water after the experi-

ment. The difference in weight is the weight of the water formed. Knowing the loss in the weight of the copper oxide, we know the weight of the oxygen required to form the amount of water obtained. The difference between the weight of the water and the weight of the oxygen is the weight of the hydrogen required to form the water. It will be found that water is composed approximately of one part by weight of hydrogen and eight parts by weight of oxygen. (See page 37.)

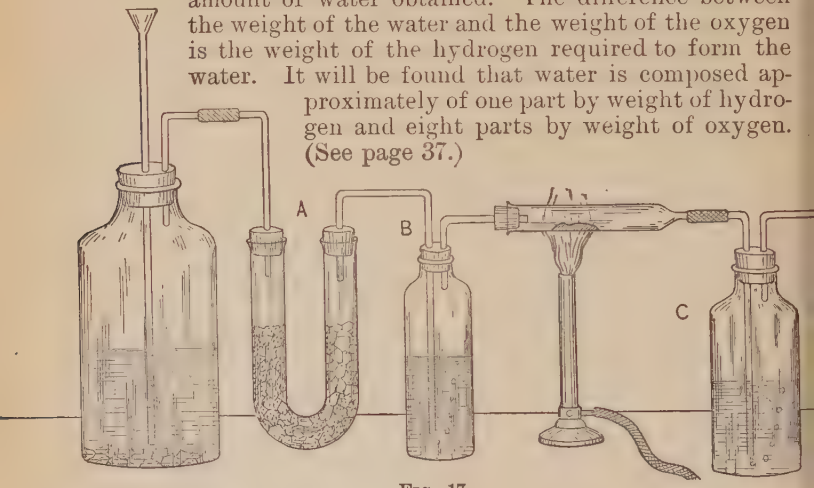

FIG. 17.

Experiment 22. Efflorescence of Sodium Sulphate. — (A few transparent crystals of sodium sulphate, and a small beaker or crystallizing dish.)

Place a few crystals of sodium sulphate in a small beaker or crystallizing dish and allow them to stand exposed to the air. The crystals will lose water, become white on the surface, and opaque. (See page 38.)

Experiment 23. Deliquescence of Calcium Chloride and Phosphorus Pentoxide. — (Two small beakers or crystallizing dishes; a few lumps of calcium chloride; a few grams of the white powder, phosphorus pentoxide.)

Introduce the calcium chloride into one vessel and the phosphorus pentoxide into the other, and expose both to the air. After a time the calcium chloride will absorb enough water to dissolve it, and the whole mass will become liquid. The phosphorus pentoxide will absorb moisture from the air and become a gummy mass. The phosphorus pentoxide forms well-known compounds with water, as we shall see. (See page 38.)

CHAPTER V

CHLORINE

Occurrence and Preparation of Chlorine. — Chlorine does not occur in the free condition in nature. This is due in part to its great chemical activity. If once set free it would quickly combine again with other substances. It occurs in combination with many other elements, but especially in combination with the element sodium, as sodium chloride. The soluble chlorides do not exist on the surface of the earth, where they are subject to the influence of water, but pass into solution and are swept down into the sea. This accounts for the large amount of chlorine in sea-water.

A number of methods have been devised for preparing chlorine, but most of these are only of historical interest.

The process devised by *Deacon* consists in oxidizing hydrochloric acid by means of the oxygen of the air. Hydrochloric acid and air are passed through heated tubes containing balls of clay saturated with copper sulphate. Under these conditions the oxygen of the air unites with the hydrogen of the hydrochloric acid, forming water and liberating chlorine.

Another method for obtaining chlorine, based upon the oxidation of hydrochloric acid, is the following: —

When a compound rich in oxygen, like manganese dioxide, is heated with hydrochloric acid, the latter is oxidized to water and chlorine. A method frequently employed in making chlorine in small quantities consists in treating a mixture of sodium chloride and manganese dioxide with sulphuric acid. Hydrochloric acid is formed by the action of the sulphuric acid on the sodium chloride, and this is oxidized by the manganese dioxide liberating chlorine.

A very convenient method for obtaining chlorine in the laboratory consists in treating *bleaching-powder* with hydrochloric acid. The bleaching-powder is introduced into an ordinary Kipp apparatus, and the acid allowed to come in contact with it.

All of these methods have practically given place to the *electrolytic*, when chlorine is to be prepared on the large scale. Most of the chlorine is now prepared by the electrolysis of aqueous potassium or sodium chloride. When a solution of potassium chloride in water is electrolyzed, hydrogen separates at one pole, and chlorine at the other. The potassium remains in solution as potassium hydroxide.

Chemical Properties of Chlorine. — The yellowish green gas chlorine is chemically very active. It combines with many elements by simple contact, and often with evolution of much heat and even light, and in some cases with explosive violence.

When copper foil is brought in contact with chlorine gas, it combines with the chlorine, shown by the fact that it glows and forms chloride of copper.

When finely divided antimony is allowed to fall into a vessel containing chlorine gas, we have literally a rain of fire — each antimony particle becoming incandescent as it combines with the chlorine. Other substances, like brass, burn in chlorine only when they have been heated to an elevated temperature.

Combustion in Chlorine. — We have here examples of combination taking place between substances and chlorine, which are analogous to combustion in oxygen. In the former case, as in the latter, the combination takes place with evolution of light and heat, and the combustion in chlorine is even more energetic than in oxygen, in that it starts at ordinary temperatures. We have, then, *combustion in chlorine* just as truly as in oxygen. The term "combustion," however, as ordinarily used always refers to combination with oxygen, since we never know chlorine in the free condition unless it is specially prepared.

Action of Chlorine on Hydrogen. — Hydrogen unites with chlorine at ordinary temperatures if exposed to diffuse light, and with explosive violence if exposed to direct sunlight. A

jet of hydrogen can, however, be burned in chlorine just as it can be burned in oxygen, and a jet of chlorine can be burned in hydrogen. When hydrogen is burned in oxygen, the two gases combine, forming water. When hydrogen is burned in chlorine the two gases combine, forming the important compound hydrochloric acid, which we shall study a little later.

Action of Chlorine on Water. — Chlorine is readily soluble in water, and the resulting solution is known as *chlorine water*. Chlorine water, if kept in the dark, is a stable substance, but if exposed to the light, a deep-seated change takes place. The chlorine acts chemically upon the water, combining with the hydrogen and liberating oxygen. The resulting solution contains the hydrochloric acid formed, while the oxygen gas is liberated. Such chemical reactions which are brought about by the action of light are known as *photochemical reactions*. Since oxygen is liberated, chlorine is known as a *strong oxidizing agent*. Its oxidizing power renders chlorine one of the very best *bleaching agents* which is at our disposal. The oxygen which is set free when chlorine acts on moisture oxidizes organic coloring-matter, and leaves behind a colorless substance. This can be illustrated by bringing into the presence of chlorine gas some moist flowers or a moist piece of calico, when the color will disappear in a very short time.

Chlorine is also an excellent *disinfectant*, having an unusual power to destroy bacteria and other forms of life. This is due in part to its oxidizing action, and in part to direct combination of chlorine with the organic matter of such forms of life.

Action of Chlorine on Certain Organic Compounds. — Chlorine not only acts on elementary substances and simple compounds, but also on complex organic substances. When brought in contact with organic substances which contain hydrogen, the chlorine first replaces the hydrogen, taking its place in the molecule, and then more chlorine combines with the replaced hydrogen, forming hydrochloric acid. Such a reaction, known as *substitution*, can be illustrated by bringing a piece of filter-paper saturated with oil of turpentine into a vessel filled with

chlorine gas. A violent reaction takes place, resulting in the liberation of a large amount of finely divided carbon.

Chlorine Hydrate. — When chlorine gas is conducted into a mixture of water and ice, a crystalline compound separates. At ordinary temperatures it decomposes into chlorine and water, while at somewhat elevated temperatures the decomposition is quite rapid, resulting in a copious evolution of chlorine gas. This compound is of special historical interest in connection with the liquefaction of chlorine. The earlier work on the liquefaction of gases was carried out almost exclusively by the great English physicist, Faraday. He succeeded in liquefying chlorine obtained from chlorine hydrate. Some of this compound was placed in one end of a thick-walled glass tube, and the other end closed, as shown in Figure 18. The end of the tube containing the chlorine hydrate was gently warmed, while the other end was surrounded by a freezing-mixture of ice and salt. Under these conditions the chlorine was liberated, and produced a pressure in the tube which was sufficient to liquefy it. Considerable precaution is necessary in carrying out this experiment, since an explosion is liable to result.

Fig. 18.

Certain Physical Properties of Chlorine. — The yellowish green gas, chlorine, is about two and one-half times as heavy as the air, a litre weighing 3.22 grams. It has a most disagreeable odor, and an injurious effect when inhaled. It acts upon the mucous membrane of the nose and throat, and disintegrates these tissues if inhaled in sufficient quantity and for sufficient time. It is therefore necessary in working with chlorine to take every precaution to be protected from the gas. Such work should always be done under a good hood, with a strong draft to remove the gas as rapidly as it escapes into the air.

Comparative Inactivity of Dry Chlorine. — While moist chlorine is one of the most active substances chemically, dry chlorine is comparatively inactive. A lecture table experiment, which is frequently shown, is to pass chlorine through a glass tube containing a piece of metallic sodium which is heated by means of a bunsen burner. If the chlorine has been carefully dried, as is frequently done, the sodium will melt and remain with untarnished surface in contact with the chlorine gas. If, on the other hand, the water-vapor has not been removed from the chlorine, vigorous chemical action will take place, accompanied by intense heat and a bright light, and the compound sodium chloride will be formed.

EXPERIMENTS WITH CHLORINE

Experiment 24. Preparation of Chlorine from Hydrochloric Acid and Manganese Dioxide. — (A two-litre balloon flask; safety-tube; rubber stopper; manganese dioxide; hydrochloric acid.)

Arrange an apparatus as in Figure 19. Into the flask *A* introduce some coarse-grained manganese dioxide. Pour hydrochloric acid through the safety-tube until the dioxide is covered with the liquid. Heat gently; chlorine is set free. The gas may be passed through water in a cylinder to remove all traces of hydrochloric acid, and can be collected from the tube. This, and all experiments with chlorine, should be performed under a good

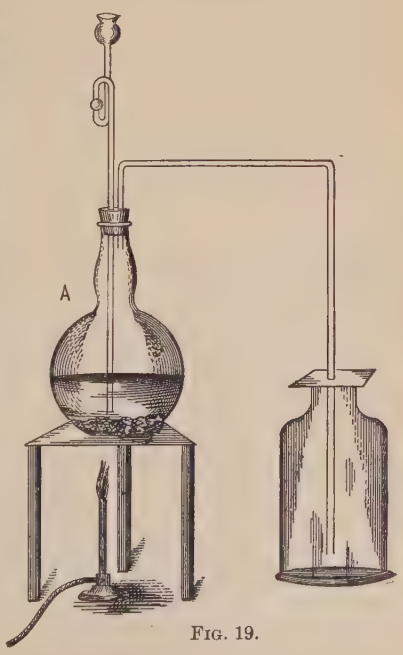

FIG. 19.

hood with a strong draft. Any chlorine not collected should be conducted into a solution of caustic potash. (See page 43.)

Experiment 25. Preparation of Chlorine by the Action of Hydrochloric Acid on Potassium Dichromate. — (Same apparatus as in last experiment. In addition some potassium dichromate.)

Arrange the apparatus exactly as in the preceding experiment. Introduce into the flask *A* 50 or 60 grams of potassium dichromate which has been coarsely pulverized. Pour into the flask through the thistle tube 200 to 250 grams of concentrated hydrochloric acid. Warm gently the contents of the flask. An abundance of pure chlorine can be obtained by this method.

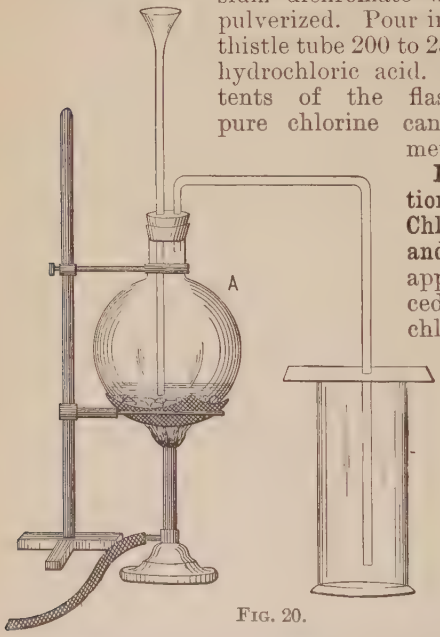

FIG. 20.

Experiment 26. Preparation of Chlorine from Sodium Chloride, Manganese Dioxide, and Sulphuric Acid. — (Same apparatus as in the preceding experiment; sodium chloride; sulphuric acid containing two parts by weight of acid to one of water.)

Arrange an apparatus as in Figure 20. Introduce into the flask *A* a mixture of 50 grams of sodium chloride and 50 grams of finely powdered manganese dioxide. Pour into the flask through the safety-tube 50 cc. of the sulphuric acid, obtained by adding two parts by weight of the concentrated acid to one of water and allowing the mixture to cool. When gently heated an abundance of chlorine is obtained.

Fill a number of cylinders or wide-mouthed bottles with the gas, by allowing the tube from which the chlorine escapes to reach to the bottom of the receiving vessel. The chlorine being heavier than air will displace the latter and fill the vessel. It is well to cover the vessel which is to be filled with chlorine with a perforated glass plate through which the de-

livery tube is passed. In this way air currents are avoided, and the vessel can be more perfectly filled with the pure chlorine. The vessels thus filled with the gas should be set aside for use in the following experiments. (See page 43.)

Experiment 27. Bleaching Action of Chlorine. — (Vessel filled with chlorine; flowers; colored fabric; etc.)

Moisten the flowers, or the fabric, and introduce into the chlorine. After a time the color will be practically destroyed. (See page 45.)

Experiment 28. Combination of Chlorine with the Metals. — (Three vessels filled with chlorine; thin copper foil; Dutch leaf; powdered antimony.)

Into one vessel filled with chlorine introduce the copper foil, into another the antimony powder, and into the third Dutch leaf. There is abundant evidence of the combination of the chlorine with the metals. (See page 44.)

Experiment 29. Action of Chlorine on Organic Compounds containing Hydrogen. — (Vessel filled with chlorine; filter-paper; oil of turpentine.)

Dip a strip of filter-paper into warm oil of turpentine and introduce into a vessel filled with chlorine. A vigorous reaction will take place, resulting in the liberation of a large amount of carbon which will cover the walls of the vessel. (See page 45.)

Experiment 30. Action of Light on Chlorine Water. — (Long glass tube 2 to $2\frac{1}{2}$ cm. in diameter; chlorine water.)

Fill a glass tube with chlorine water, obtained by saturating cold water with chlorine. Expose the tube to diffuse light and to ordinary sunlight and observe the bubbles of oxygen rise in the tube and collect at the top. (See page 45.)

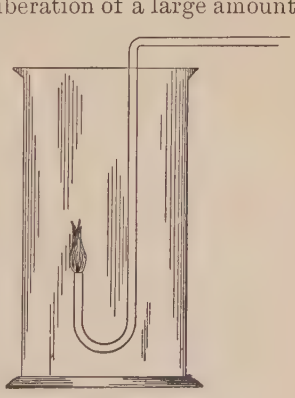

FIG. 21.

Experiment 31. Burning Hydrogen in Chlorine. — (Cylinder filled with chlorine; hydrogen generator.)

Arrange the apparatus as shown in Figure 21. The hydrogen escaping from the tube is ignited and lowered into the chlorine. The hydrogen burns with a light blue flame, and vapors of hydrochloric acid escape. This can be seen at the mouth of the cylinder, or tested by a piece of moistened blue litmus paper, which is turned red. (See page 44.)

CHAPTER VI

LAWS OF CHEMICAL ACTION

The study of chemical phenomena consisted at first in simple observation and description. Two substances were allowed to react chemically and the reaction was observed. The nature and properties of the substances entering into the reaction were studied, and then the nature and properties of the products formed. This was the qualitative stage of chemistry.

Mere qualitative observations are followed by quantitative measurements in the development of any branch of natural science.

The quantities of the substances which enter into a reaction were carefully weighed, and the quantities of the products formed. The amounts of different substances which combine with one another were determined, and certain other changes which take place simultaneously with chemical transformations were studied. Still we do not have a science. Indeed, the highest aim of a science is not simply to observe and record facts.

Generalization. — The highest aim of scientific investigation is the discovery of wide-reaching relations between large numbers of facts. Such relations when sufficiently comprehensive are known as generalizations. A simple example by way of illustration. It was early observed that a body thrown upward from the surface of the earth will return again to the surface. Repeated observations confirmed those first made, but it remained for Newton to arrive at the generalization known as the law of gravitation.

lie at the foundation of the science of chemistry. Were we to stop here we should leave untouched a class of phenomena whose importance cannot easily be overestimated.

Whenever we have chemical reaction taking place we have *heat liberated or absorbed, and usually liberated.* This brings us to a study of the *energy changes* which are inseparably connected with all chemical action.

Energy manifests itself in a number of forms. We have *light energy, heat energy, electrical energy, mechanical energy,* and these are mutually convertible into one another. That mechanical energy can be converted into heat is shown wherever friction exists. Rub together two pieces of metal and both become hot. That heat energy can be converted into light energy is illustrated by a piece of metal which has been heated to incandescence. This principle of the mutual convertibility of the various forms of energy is known as the *principle of the correlation of energy,* and is an important generalization in physical science.

That one form of energy can be converted *qualitatively* into another is important, but far less important than the fact that one form of energy can be converted *quantitatively* into another. When, for example, mechanical energy disappears, as when a hammer falls upon a metal plate, the heat energy produced is exactly equivalent to the mechanical energy which has disappeared. If the heat energy produced under these conditions was transformed into work, it would raise the hammer again exactly to its original position. This principle, fundamental to the science of physics, is known as the *principle of the conservation of energy.* It says in words that no energy can be created or lost, and is analogous to the law of the conservation of mass, which we have already studied.

Importance of the Conservation of Energy for the Science of Chemistry. — The bearing of the conservation of energy upon chemistry may not appear at first sight. In addition to the forms of energy enumerated above we should add *intrinsic energy,* which is frequently referred to as *chemical energy.* This

form of energy exists in all substances in larger or smaller amounts, and is the form which is converted into heat when a piece of coal is burned. The existence of this form of energy is essential to all chemical action, and is, therefore, absolutely essential to the science of chemistry.

Although only a part of the intrinsic or chemical energy in the substances which react is converted into heat or some other form of energy during the reaction, yet this part which disappears is converted quantitatively into other forms. The law of the conservation of energy is, therefore, fundamental to the scientific study of chemistry.

Chemical Formulas and Chemical Equations. — The formula for any chemical compound is the symbols of the elements in the compound written side by side. Thus, the formula for water is H_2O. This means that the molecule, or the smallest particle of the compound of water, is made up of two atoms of hydrogen and one atom of oxygen. The formula for manganese dioxide is MnO_2, which means that the molecule or smallest particle of the compound contains one atom of manganese and two atoms of oxygen. The formula for potassium chlorate is $KClO_3$, the molecule containing one atom of potassium, one atom of chlorine, and three atoms of oxygen.

Chemical reactions are expressed by chemical equations, as we say. The term "equation" is used because the same kinds and amounts of matter must appear on both sides of it.

Take the reaction between hydrogen and chlorine. This is expressed by the following equation: —

$$^{1}\,H_2 + Cl_2 = 2\,HCl,$$

which means that two atoms of hydrogen unite with two atoms of chlorine and form two molecules of hydrochloric acid.

[1] It is impossible to explain until later the reason for using the apparent double quantities of the elements in this and subsequent equations. It is, however, better to learn the true equations at once, even if their full significance cannot be seen until a little more progress has been made in the subject.

The reaction between hydrogen and oxygen is expressed by the following equation: —

$$2\ H_2 + O_2 = 2\ H_2O.$$

This means that four atoms of hydrogen unite with two atoms of oxygen and form two molecules of water.

In a similar manner chemical reactions in general can be expressed by equations, which, in some cases, are quite complex. We can now write the equations for the reactions already studied. The equation in any case does not tell us simply what elements enter into a reaction, but the quantities of the different elements that react, and the number of atoms of the different elements in the various substances involved in the reaction. This will be seen in the following examples.

Equations involved in the Study of Oxygen. — The formation of oxygen from potassium chlorate may be represented by the following equation: —

$$2\ KClO_3 = 2\ KCl + 3\ O_2.$$

When oxygen is formed by heating manganese dioxide, we have: —

$$3\ MnO_2 = Mn_3O_4 + O_2.$$

The formation of oxygen from mercuric oxide is represented thus: —

$$2\ HgO = 2\ Hg + O_2;$$

while the reaction between hydrogen dioxide and lead dioxide may be formulated thus: —

$$H_2O_2 + PbO_2 = PbO + H_2O + O_2.$$

When sulphur burns in oxygen, we have: —

$$S + O_2 = SO_2.$$

The combustion of iron is represented thus: —

$$3\ Fe + 2\ O_2 = Fe_3O_4.$$

Carbon burns in oxygen, forming carbon dioxide: —

$$C + O_2 = CO_2;$$

while phosphorus forms the pentoxide: —

$$4\ P + 5\ O_2 = 2\ P_2O_5.$$

Equations involved in the Study of Hydrogen. — The following equation represents the reaction between sodium and water: —

$$2\ Na + 2\ H_2O = 2\ NaOH + H_2.$$

When hydrochloric acid acts on zinc, we have: —

$$2\ HCl + Zn = ZnCl_2 + H_2.$$

When sulphuric acid acts on zinc: —

$$H_2SO_4 + Zn = ZnSO_4 + H_2.$$

The reaction between hydrogen and oxygen may be represented thus: —

$$2\ H_2 + O_2 = 2\ H_2O.$$

The reduction of copper oxide by hydrogen is formulated as follows: —

$$CuO + H_2 = Cu + H_2O.$$

The decomposition of water by the electric current can be represented thus: —

$$2\ H_2O = 2\ H_2 + O_2.$$

Equations involved in the Study of Chlorine. — When hydrochloric acid is oxidized by the oxygen of the air: —

$$4\ HCl + O_2 = 2\ H_2O + 2\ Cl_2.$$

When it is oxidized by manganese dioxide: —

$$4\ HCl + MnO_2 = 2\ H_2O + MnCl_2 + Cl_2.$$

The reaction when sodium chloride is treated with sulphuric acid in the presence of manganese dioxide is more complicated and may be represented as taking place in two stages: —

$$\text{I.} \quad 2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$$
$$\text{II.} \quad 2\,HCl + MnO_2 + H_2SO_4 = MnSO_4 + 2\,H_2O + Cl_2.$$

Representing both reactions in one equation, we have: —

$$2\,NaCl + MnO_2 + 2\,H_2SO_4 = MnSO_4 + Na_2SO_4 + 2\,H_2O + Cl_2.$$

The reaction between hydrochloric acid and potassium dichromate, giving free chlorine, may be formulated thus: —

$$K_2Cr_2O_7 + 14\,HCl = 2\,KCl + 2\,CrCl_3 + 7\,H_2O + 3\,Cl_2.$$

The reaction between copper and chlorine may be represented thus: —

$$Cu + Cl_2 = CuCl_2.$$

Between antimony and chlorine thus: —

$$2\,Sb + 3\,Cl_2 = 2\,SbCl_3.$$

The combination of chlorine and hydrogen is represented very simply: —

$$H_2 + Cl_2 = 2\,HCl;$$

while the reaction of chlorine with water is a little more complex: —

$$2\,Cl_2 + 2\,H_2O = 4\,HCl + O_2.$$

The action of chlorine on organic compounds is much more complicated.

CHAPTER VII

OZONE AND HYDROGEN DIOXIDE

OZONE

Allotropic Modification of Oxygen. — We have dealt thus far with the element oxygen in the condition in which it is ordinarily known to us. Oxygen can, however, occur with properties very different from ordinary oxygen. The second modification of oxygen is known as *ozone*. The property of an element to occur in two different modifications is known as *allotropy*, and ozone is spoken of as an allotropic modification of oxygen.

Preparation of Ozone. — Ozone is formed in larger or smaller quantities under a number of conditions. When phosphorus

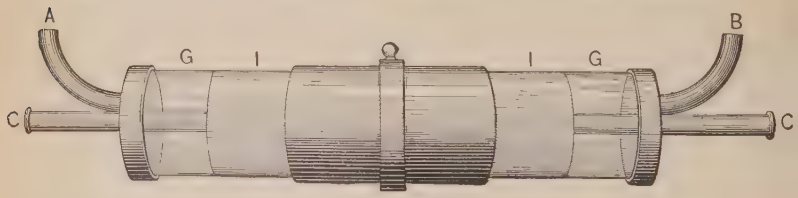

Fig. 22.

is exposed to the air it undergoes slow oxidation, and at the same time some of the oxygen of the air is converted into ozone.

The best method of obtaining ozone in quantity is by passing electricity through oxygen.

A convenient form of apparatus for preparing ozone is the following (Fig. 22): Into the glass tube *GG* an iron tube *II* is inserted. The glass tube is surrounded for a part of its length

by tin-foil. Oxygen is introduced into the glass tube through the tube *A* and escapes through *B*. A current of water is passed through the tube *CC* to keep the apparatus cool. The tin-foil, on the one hand, and the tube *C*, on the other, are connected with the poles of an induction machine. Silent discharges take place between the tin-foil and the iron, passing through the oxygen. Under these conditions a part of the oxygen is converted into ozone.

Properties of Ozone. — Ozone is, in general, a much more active substance chemically than oxygen, having a much greater oxidizing power, especially at low temperatures. Thus, ozone will oxidize metallic silver at ordinary temperatures, covering it with a layer of brown oxide, while under similar conditions oxygen is not able to effect such an oxidation. Ozone is detected most easily by its action on a colorless solution of potassium iodide. Such a solution becomes brown when brought in contact with ozone, due to the liberation of iodine.

Transformation of Ozone into Oxygen. — We have seen that oxygen is transformed into ozone under the influence of the silent electrical discharge. The question naturally arises, Can ozone once formed be transformed again into oxygen? The answer is, it can. When ozone is heated to 300°, it passes back into ordinary oxygen. We can thus pass either from oxygen to ozone or from ozone to oxygen.

This raises the important question, What is the cause of the difference in properties between the two modifications of oxygen?

The Same Kind of Matter but Different Amounts of Energy. — We have already seen that oxygen and ozone are made up of the same kind of matter, since each is transformable into the other. If we study this side of the problem quantitatively, we shall find that when three volumes of oxygen are converted into ozone, the resulting gas occupies only two volumes. Thus, if three litres of oxygen were converted into ozone, only two litres of ozone would be formed. On the other hand, if two

litres of ozone were decomposed by heat, three litres of oxygen would be formed.

To anticipate what we shall understand more clearly later, the atom of oxygen cannot exist by itself in the free state, but two atoms of oxygen always unite and form what is called the molecule of oxygen. In oxygen gas, as we ordinarily know it, we do not have the atoms of oxygen uncombined with one another, but the molecules which are formed by the union of two atoms.

It has been shown that in the molecule of ozone there are three atoms of oxygen, while in the molecule of oxygen there are only two. It is obvious, however, that the difference in the number of atoms in the molecule, alone considered, is not sufficient to account for such differences in properties as exist between oxygen and ozone. Indeed, it is difficult to see how this would produce a difference in any property other than the mass of the molecule.

The real difference in the properties of oxygen and ozone is due to the different amounts of intrinsic energy present in their molecules. This statement is not made dogmatically, but can be demonstrated experimentally in the following manner: —

When carbon is burned in oxygen the product is carbon dioxide. When carbon is burned in ozone the product is carbon dioxide. We start with the same substance, carbon, in both cases, and we end with the same product, carbon dioxide. Any differences in the two reactions must be due to the differences between the oxygen and the ozone.

If we measure the *amounts of heat* liberated in the two reactions, we find that they are very different indeed. Considerably more heat is evolved when carbon is burned in ozone than when carbon is burned in oxygen. This shows that there is *more intrinsic energy present in the molecule of ozone than in the molecule of oxygen.*

HYDROGEN DIOXIDE

Hydrogen Dioxide. — One compound of hydrogen and oxygen, other than water, calls for special comment. This is the compound *hydrogen dioxide.* It has the composition expressed by the formula H_2O_2, and is, therefore, an oxidized water. Hydrogen dioxide is most readily prepared in quantity by treating the compound barium dioxide, with an acid. If we use hydrochloric acid, the equation is expressed thus: —

$$BaO_2 + 2\,HCl = BaCl_2 + H_2O_2.$$

Properties of Hydrogen Dioxide. — Hydrogen dioxide is a colorless, viscous liquid, much heavier than water, having a specific gravity of 1.4996. We saw that water in thick layers has a markedly bluish tint. Hydrogen dioxide is still deeper blue when observed in thick layers.

One of the characteristic properties of hydrogen dioxide is the ease with which it decomposes into water and oxygen.

$$2\,H_2O_2 = 2\,H_2O + O_2.$$

On account of the ease with which hydrogen dioxide gives up oxygen it is a good oxidizing agent. If brought in contact with substances which can take up oxygen, it parts with it readily, and such substances are oxidized. Upon this fact is based its value as a *disinfectant.* When brought in contact with organic matter it oxidizes it and destroys its vitality. Bacteria and other germs which produce disease are thus destroyed by hydrogen dioxide.

CHAPTER VIII

COMPOUNDS OF CHLORINE WITH HYDROGEN AND OXYGEN

Hydrochloric Acid, HCl. — The compound formed by the union of hydrogen with chlorine is known as *hydrochloric acid.* This compound is formed when hydrogen is burned in chlorine. The same compound is formed when a mixture of hydrogen and chlorine is exposed to diffuse light. When the mixture is exposed to direct sunlight they combine with explosive violence.

Volume Relations in which Hydrogen and Chlorine combine. — It will be remembered that one volume of oxygen combines with two volumes of hydrogen, and forms two volumes of water-vapor. The relations which obtain in the case of hydrogen and chlorine are even simpler. When one volume of hydrogen is mixed with one volume of chlorine and combination takes place, all of both gases are used up, and just two volumes of hydrochloric acid are formed. The law of the simple volume relations in which gases combine holds here even more strikingly than in the case of oxygen and hydrogen.

Preparation of Hydrochloric Acid. — Hydrochloric acid gas is prepared most conveniently, as follows: When a salt of hydrochloric acid is treated with a non-volatile acid such as sulphuric, hydrochloric acid gas is set free. The best known salt of hydrochloric acid is, as we have seen, sodium chloride. When this is treated with sulphuric acid, a reaction takes place in the sense of the following equation: —

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$$

The hydrochloric acid gas thus formed is conducted into water, which has the power of absorbing large quantities of

it. This is the form in which it is used in the laboratory and in the arts.

Chemical Properties of Hydrochloric Acid. — Hydrochloric acid, as the name implies, is an acid, and since this is the first substance which we have thus far encountered with acid properties (say the power to color blue litmus red), a few words should be added in reference to acids in general. Hydrochloric acid has the composition represented by the formula HCl. Its molecule therefore contains one atom of hydrogen and one of chlorine. The question arises to which constituent are the acid properties due? It may be due to either or to both. When we come to study other acids we shall learn that many substances are acids which do not contain chlorine, and many compounds containing chlorine are not acids, therefore, chlorine is not essential to acidity. We shall also learn that all substances which are acid contain hydrogen, and no other element in common. Hydrogen is therefore essential to acidity.

There are, however, many compounds which contain hydrogen and which are not acids. The question which arises is, How does the hydrogen in the latter class of compounds differ from the hydrogen in the former?

The Theory of Electrolytic Dissociation. — It is obvious that the atomic theory does not enable us to answer questions like the above. In terms of this theory one atom of hydrogen is like any other atom of hydrogen, and the chemical behavior of all atoms of hydrogen should be the same. The fact is they are very different, and we must, therefore, supplement the atomic theory in order to be able to account for these differences.

When a substance like hydrochloric acid is dissolved in water, all the properties of the solution show that there is a larger number of parts in the solution than would correspond to the molecules of the compound. It would lead us too far in this connection to discuss the various physical chemical methods by which this conclusion is established. Suffice it to say here that this conclusion is reached as the result of the

application of several independent methods, and is established beyond question.

Since a solution of hydrochloric acid contains a larger number of parts than would correspond to the molecules of the compound, it is obvious that the molecules in solution must be broken down into simpler parts. In the case of hydrochloric acid the only parts into which the molecule could break down are hydrogen and chlorine.

Such a solution is capable of conducting the electric current, and the only way in which a solution can conduct the current is for the dissolved particles to carry an electrical charge. Molecules in solution do not conduct the current, shown by the fact that solutions of cane sugar, alcohol, and the like are non-conductors. The parts into which the molecules of hydrochloric acid break down are, therefore, charged, and thus differ from ordinary hydrogen and chlorine, which are uncharged. These charged parts are known as *ions*. The ions which are charged positively are known as *cations*, while those which are charged negatively are known as *anions*. When a molecule breaks down or dissociates as we say in the presence of a solvent like water, one part of the molecule is always charged positively or is a cation, while the other part is always charged negatively or is an anion. This theory of the dissociation of molecules into ions is known as the *theory of electrolytic dissociation*.

Importance of the Theory of Electrolytic Dissociation for Chemistry. — It is obvious from the above that the atomic theory has been supplemented by a new conception. In addition to the conception of the atom we have now that of the atom carrying an electrical charge. The question may fairly be asked, why bring in this new idea? The answer is, first, because it is true. We have an overwhelming amount of evidence in favor of the theory of electrolytic dissociation, most of which, obviously, cannot be presented here. It can, however, be shown that molecules, in general, cannot react chemically. Dissolve hydrochloric acid gas in some solvent like

benzene, which does not have the property to any marked degree of breaking down the molecules of the acid into ions. *Such a solution has only slightly acid properties.* It does not color blue litmus red. It is obvious that in such a solution we have an abundance of molecules of hydrochloric acid, and yet such slight acid properties. The molecules, then, do not have acid properties.

Again, take pure, dry, liquid hydrochloric acid. We have here a great abundance of molecules of hydrochloric acid, and yet *no acid properties.*

On the other hand, wherever we have the molecules of hydrochloric acid dissociated into ions we have acid properties manifesting themselves to a marked extent.

The relations pointed out for hydrochloric acid hold for most chemical substances. The molecules are relatively inert; *the ions being the active agents chemically.* It is thus obvious that the theory of electrolytic dissociation is of fundamental importance for the whole science of chemistry.

Method of Indicating the Existence of Ions. — As we shall have to deal frequently with ions, we adopt some method of distinguishing between atoms and ions. Since ions are charged atoms or groups of atoms, we shall use the positive sign over the symbol of an atom to mean that it is charged positively, or is a *cation.* The negative sign over an atom or group of atoms means that it is carrying a negative charge and is an *anion.* Hydrochloric acid is dissociated by water in the sense of the following equation: —

$$HCl = \overset{+}{H}, \overset{-}{Cl}.$$

The comma between the two ions means that they come from the same molecule, and will unite again and form the original molecule when the water is removed. This method of expressing the dissociation of molecules into ions is adopted throughout the book.

Action of Hydrochloric Acid on a Metal like Zinc. — When a solution of hydrochloric acid is brought in contact with a metal

like zinc, the latter takes the positive charge from the hydrogen ion, becoming itself an ion and passing into solution, while the hydrogen ion having lost its electrical charge becomes an atom. Two atoms of hydrogen then combine and form a molecule. The reaction between zinc and hydrochloric acid is represented by the following equation: —

$$Zn + \overset{+}{H},\ \overset{-}{Cl} + \overset{+}{H},\ \overset{-}{Cl} = \overset{++}{Zn},\ \overset{-}{Cl},\ \overset{-}{Cl} + H_2.$$

Hydrochloric acid acts upon metals in general in the sense of the above equation — the metal taking the charge from the hydrogen ion, becoming itself an ion, converting the hydrogen into the atomic condition, and this then passes into the molecular condition.

Definition of an Acid. — Having studied hydrochloric acid as the type of a large class of chemical compounds known as *acids*, we are prepared to consider these a little more closely.

All acids have certain properties in common. They all taste sour; they have the property of coloring certain vegetable dyes red; they all contain hydrogen which can give up its electrical charge to certain metals, itself escaping as hydrogen gas.

Hydrogen in this form is known as *ionic hydrogen*, and, as has been stated, wherever we have ionic hydrogen we have acid properties, and wherever we have acid properties we have ionic hydrogen. To say that a compound has acid properties means, then, that *when it is dissolved in water or some other dissociating solvent it yields hydrogen ions.*

This definition says that a compound is not an acid unless it is brought into the presence of a dissociating solvent. This is the same as to say that no pure, homogeneous substance is an acid.

We shall learn that the above relations hold for all acids. No pure, dry, homogeneous substance is an acid. It becomes an acid only when dissociated by a solvent or some other means into hydrogen cations, and into anions whose nature depends upon the acid in question and varies with every acid.

Detection of Hydrochloric Acid. — There is one reaction which serves to detect hydrochloric acid under all ordinary conditions. Hydrochloric acid is, as we have seen, dissociated into hydrogen ions and chlorine ions.

To detect hydrochloric acid we must make use of some reaction which is characteristic of the chlorine ion, since all acids yield hydrogen ions. Such a reaction takes place whenever a silver ion is brought in contact with a chlorine ion.

$$\overset{+}{\mathrm{H}},\ \overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{Ag}},\ \overset{-}{\mathrm{NO_3}} = \mathrm{AgCl} + \overset{+}{\mathrm{H}},\ \overset{-}{\mathrm{NO_3}}$$

expresses the reaction between hydrochloric acid and silver nitrate. The silver chloride formed is a white solid, readily soluble in ammonia. Since soluble chlorides in general yield in solution chlorine ions, this is a means of detecting also the presence of such chlorides.

Physical Properties of Hydrochloric Acid. — Hydrochloric acid is a colorless gas, with a sharp, pungent odor, and produces marked irritation of the mucous membrane of the nose and throat when inhaled even in small quantity. The gas shows unusual solubility in water, one volume of water at zero degrees dissolving about 503 volumes of the gas. The gas has such great attraction for water that if the breath is blown across the open mouth of a bottle of concentrated hydrochloric acid, the particles of water are condensed by the escaping hydrochloric acid and a mist is produced, which can be readily seen. The same effect is observed when the breath is blown into a stream of hydrochloric acid gas escaping from a generator.

Aqueous Solution of Hydrochloric Acid. — The hydrochloric acid that is used in the laboratory is a solution of the gas in water. The concentration of the solution increases as more and more gas is dissolved.

Compounds of Chlorine with Oxygen. — Although chlorine and oxygen cannot be made to combine directly, several compounds of these two elements have been made by indirect

methods. These compounds are chlorine monoxide (Cl_2O), chlorine dioxide (ClO_2), and chlorine septoxide (Cl_2O_7). These compounds are all characterized by instability.

Compounds of Chlorine with Hydrogen and Oxygen. — Thus far we have studied compounds between only two elements. We might suspect, therefore, that only two chemical elements can combine with one another, forming a definite molecule, or at least that this is by far the most common form of chemical union. Such is by no means the case. We shall now study briefly a class of compounds between the three elements, chlorine, oxygen, and hydrogen, which, if not very common substances, have considerable chemical interest. These compounds are: —

Hypochlorous acid	$HClO$.
Chlorous acid	$HClO_2$.
Chloric acid	$HClO_3$.
Perchloric acid	$HClO_4$.

Hypochlorous Acid, HOCl. — When chlorine is conducted into a cold, dilute solution of potassium hydroxide, the reaction takes place in the sense of the following equation: —

$$2\,KOH + Cl_2 = KCl + KOCl + H_2O.$$

The salts of hypochlorous acid are termed *hypochlorites*. This salt is, therefore, potassium hypochlorite.

When this salt is treated with a cold, dilute solution of hydrochloric acid, the hypochlorous acid is set free: —

$$KOCl + HCl = KCl + HOCl.$$

The hypochlorous acid can then be distilled off and collected.

Calcium Hypochlorite, $Ca(OCl)_2$. — The calcium salt of hypochlorous acid is used extensively as a bleaching agent on account of the ease with which it gives up chlorine. When chlorine is passed into slaked lime, the following reaction apparently takes place: —

$$2\,Ca(OH)_2 + 2\,Cl_2 = CaCl_2 + Ca(OCl)_2 + 2\,H_2O.$$

This apparent mixture of calcium chloride and calcium hypochlorite is known as *bleaching-powder*, and is largely used as a disinfectant.

Chloric Acid, $HClO_3$. — When chlorine gas is conducted into a hot, concentrated solution of potassium hydroxide, the following reaction takes place: —

$$6\,KOH + 3\,Cl_2 = 5\,KCl + KClO_3 + 3\,H_2O.$$

The solution contains, after the reaction is over, two salts, potassium chloride and potassium chlorate. These can, however, be readily separated by their different solubilities in water — potassium chloride being quite soluble, while potassium chlorate is very much less soluble.

From the solution potassium chlorate readily crystallizes, especially on evaporation, leaving behind in solution the potassium chloride. With potassium chlorate we have already become somewhat familiar when we were studying methods of preparing oxygen. It will be remembered that this compound gives off all of its oxygen when heated to an elevated temperature.

When potassium chlorate is treated with a dilute solution of sulphuric acid, the following reaction takes place: —

$$2\,KClO_3 + H_2SO_4 = K_2SO_4 + 2\,HClO_3.$$

Care must be taken not to treat potassium chlorate with concentrated sulphuric acid, since violent explosions almost always result.

The solution contains the chloric acid, but since the latter cannot be distilled without undergoing decomposition, this method does not yield pure chloric acid.

To obtain pure chloric acid a salt of this acid must be used which will form an insoluble precipitate with sulphuric acid. The barium salt is the most convenient. When barium chlorate is treated with a dilute solution of sulphuric acid in equivalent quantity, insoluble barium sulphate is precipitated, and pure chloric acid remains in solution.

$$Ba(ClO_3)_2 + H_2SO_4 = \underset{\text{(Insoluble)}}{BaSO_4} + 2\,HClO_3.$$

The barium sulphate is then filtered off, or the clear, supernatant liquid decanted from the precipitate and concentrated in a vacuum or over sulphuric acid.

Properties of Chloric Acid. — Chloric acid is a colorless liquid, with very strongly acid properties and with great oxidizing power. It contains a large amount of oxygen, which it readily gives up. When a piece of paper is saturated with a concentrated solution of chloric acid, it is oxidized so energetically that it bursts into flame.

Chlorates. — The chlorates, as the salts of chloric acid are called, are very energetic oxidizing agents. This is due in part to the large amount of oxygen which they contain, and in part to the ease with which they give it up.

The Chlorine Ion and the Ion of Chlorates. — We have studied one of the characteristic properties of the chlorine ion, viz. its power to combine with the silver ion and form insoluble silver chloride. We would naturally ask whether the chlorine in potassium chlorate has this same power. Potassium chlorate dissociates as follows: —

$$KClO_3 = \overset{+}{K},\ \overset{-}{ClO_3}.$$

Chlorine in this case, instead of forming the anion, forms only a part of the anion. It is in combination with three oxygen atoms, and the chlorine and oxygen form the anion. If a solution of potassium chlorate is treated with a solution of silver nitrate, no precipitate is formed; showing that chlorine has very different properties when alone in the ionic state, than when combined with another element forming part of a complex ion.

Perchloric Acid, $HClO_4$. — When potassium chlorate is heated vigorously, it gives off all of its oxygen, as we saw when we were studying methods for the preparation of oxygen. If, however, potassium chlorate is heated moderately, it gives off only a part of its oxygen.

$$2\,KClO_3 = KCl + KClO_4 + O_2.$$

The perchlorate, $KClO_4$, can be obtained from the mixture by dissolving out the potassium chloride by means of cold water in which potassium chlorate is very slightly soluble.

When potassium perchlorate is treated with sulphuric acid, perchloric acid is set free.

$$2\ KClO_4 + H_2SO_4 = K_2SO_4 + 2\ HClO_4.$$

Properties of Perchloric Acid. — Perchloric acid is more stable than any of the other oxygen and hydrogen compounds of chlorine. The pure acid is a very vigorous oxidizing agent, and explodes easily when brought in contact with substances which can be oxidized.

Perchloric acid is a very strong acid, which is the same as to say that it is very much dissociated by water. It readily replaces hydrochloric acid from its salts, but this is partly due to the comparative insolubility of the perchlorates; it being a general law in chemistry that *when an insoluble compound can be formed it is formed.* If a fairly concentrated solution of potassium chloride is treated with perchloric acid, needles of potassium perchlorate are precipitated.

Valence. — Two atoms of chlorine are sometimes required to combine with one atom of oxygen, as in the compound Cl_2O. In other cases, one atom of chlorine combines with two atoms of oxygen, as in ClO_2, while in the compound Cl_2O_7, one atom of chlorine combines with three and a half atoms of oxygen. The power of an atom to hold other atoms in combination is known as its valence. This is not to be taken as a definition, but simply as a description of the action of chemical valence.

We have already seen examples of chemical action taking place between ions, which are atoms or groups of atoms charged with electricity. There is abundant evidence that nearly all chemical action is between ions or charged parts. The establishment of this fact has given us a definite physical basis for the conception of valence.

An ion is *univalent*, or can combine with one hydrogen atom, which is really the unit of valence, if it carries one electrical

charge. An ion is *bivalent*, or can combine with two hydrog atoms, which are equivalent under all ordinary conditions one oxygen atom, if it carries two electrical charges; *trivale* if it carries three charges; *quadrivalent*, if it carries fo charges; *quinquivalent*, if there are five charges upon it; *se ivalent*, if it carries six charges; *septivalent*, if there are sev charges connected with it; and *octivalent*, if it carries eig charges. There are no ions known which have a greater va ence than eight; *i.e.* which have the power of combining wi more than eight hydrogen atoms, or four oxygen atoms.

Faraday's Law the Basis of Chemical Valence. — Farad passed an electric current through a solution of an electroly and observed that the amount of the electrolyte decomposed w proportional to the amount of current which had passed throu the solution. On the basis of this experimentally establish fact he enunciated the first part of his well-known law: —

The amount of chemical decomposition effected by the passa of the current is proportional to the amount of electricity wh flows through the conductor.

Since electricity can flow through a solution of an electroly only by being carried by the ions in the solution, the above pa of Faraday's law shows that each ion of the same substan carries exactly the same amount of electrical energy.

Faraday determined also the amounts of different elemen which are separated from their compounds, by passing t same current through solutions of these compounds. A ge eralization of very wide significance was reached, which is t second part of the law of Faraday: —

The amounts of the different elements which are separated the same quantity of electricity bear the same relation to one other as the equivalents of these elements.

This is saying in other words that all univalent eleme carry exactly the same quantity of electricity, all bivalent e ments carry exactly twice this quantity, all trivalent eleme

three times the quantity, and so on. In a word, all univalent ions carry the same amount of electricity, and all polyvalent ions a simple, rational multiple of the amount carried by univalent ions — the multiple being the valence of the ion.

EXPERIMENTS WITH THE COMPOUNDS OF CHLORINE WITH HYDROGEN AND OXYGEN

Experiment 32. Preparation of Hydrochloric Acid by the Action of Sulphuric Acid on Sodium Chloride. — (Same apparatus as in Experiment 26; sodium chloride; sulphuric acid containing by volume 2 parts of acid to 1 of water.)

Arrange an apparatus as in Experiment 26. Introduce into the flask *A* 60 grams of sodium chloride. Pour in gradually and cautiously about 75 grams of the acid of the concentration given above. Warm gently. Hydrochloric acid will be given off in abundance. Vessels can be filled with hydrochloric acid in the same manner that they were filled with chlorine, since the gas is heavier than air. Fill a number of cylinders and bottles with the gas for further experiments. (See page 62.)

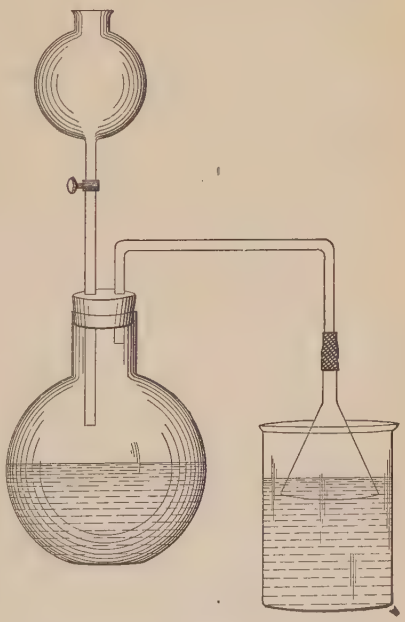

FIG. 23.

Experiment 33. Preparation of Hydrochloric Acid Gas by the Action of Concentrated Sulphuric Acid on a Concentrated Aqueous Solution of Hydrochloric Acid. — (Dropping-funnel; 500 cc. flask; exit-tube; rubber stopper; small funnel; concentrated hydrochloric acid; concentrated sulphuric acid.)

Arrange the apparatus as shown in Figure 23. Allow the

sulphuric acid to drop very slowly into the concentrated hydrochloric acid. Collect the gas in water, allowing the funnel at the end of the exit-tube to dip just beneath the surface of the water. Preserve the aqueous solution of hydrochloric acid for further experiments.

Place a thermometer in the water before the gas is conducted in, and observe the rise in temperature as the gas is absorbed.

Experiment 34. Properties of an Aqueous Solution of Hydrochloric Acid. — (Aqueous solution of hydrochloric acid; potassium hydroxide; solution of litmus; alcoholic solution of phenolphthalein; piece of zinc; solution of silver nitrate.)

Add some of the hydrochloric acid to a piece of zinc. Show that hydrogen escapes.

Add a drop of the solution of hydrochloric acid to silver nitrate. Observe the white precipitate formed. Add ammonia, and the white precipitate will dissolve.

Add a few drops of the solution of hydrochloric acid to much water. Taste the solution. Add a few drops of the solution of litmus and observe the red color. Add drop by drop the solution of potassium hydroxide, stirring the solution thoroughly after the addition of each drop until the solution turns blue. To the blue solution add a little more hydrochloric acid and observe the red color appear again.

To another portion of very dilute hydrochloric acid add a few drops of the alcoholic solution of phenolphthalein. The solution remains colorless. Add drop by drop potassium hydroxide. The solution becomes beautifully red. Add more of the acid, and the red color will disappear. These are some of the reactions of hydrochloric acid: Action on metals. Formation of an insoluble compound with silver nitrate. Neutralization of bases. (See page 67.)

Experiment 35. Preparation of Calcium Hypochlorite; Bleaching-powder. — (Flask holding 250 cc. lime; chlorine generator.)

Add water drop by drop to 25 grams of lime until it is just slaked, but is still a dry powder. Introduce into a flask holding 250 cc. and pass chlorine into the flask, shaking the dry slaked lime very frequently.

Bleaching-powder is formed in a short time. Treat a little with hydrochloric acid. What is given off? (See page 68.)

Experiment 36. Preparation of Potassium Chlorate. — (Chlorine generator; beaker; caustic potash.)

Dissolve 50 grams of caustic potash in 100 cc. of water and

pass chlorine into the solution as long as it is absorbed. Boil off about one-half of the liquid. Crystals of potassium chlorate are deposited from the solution when cold, together with some potassium chloride. Filter off the crystals and dissolve them in a minimum amount of hot water. Allow the solution to cool, when practically pure potassium chlorate will crystallize out.

Most of the potassium chloride formed remains in the original solution, since potassium chloride is so readily soluble in water. Evaporate the solution to about one-fourth volume, to allow most of the potassium chlorate remaining in solution to separate. Filter off this substance and evaporate the remaining solution to dryness. Potassium chloride will separate from the solution.

Test the potassium chlorate by heating a small portion in a hard-glass tube, and show that oxygen is given off.

Test the potassium chloride by treating a little in a test-tube with concentrated sulphuric acid, and show that hydrochloric acid escapes. (See page 69.)

Experiment 37. Oxidizing Power of Chloric Acid. — (Pipette; potassium chlorate; cane sugar; concentrated sulphuric acid.) (*This experiment to be performed only by the instructor.*) Mix a few grams of cane sugar with a few grams of potassium chlorate, and place the mixture on a stone slab under the hood. Add cautiously from the pipette a drop or two of concentrated sulphuric acid. The whole mass will burst into violent flame. (See page 70.)

CHAPTER IX

NITROGEN

Occurrence and Preparation. — The chief source of nitrogen is the atmospheric air, which consists approximately of one-fifth oxygen and four-fifths nitrogen.

It can be prepared in fairly pure condition by removing the oxygen from atmospheric air. This can be accomplished by means of phosphorus. When moist phosphorus is brought in contact with the air, the oxygen combines with the phosphorus, and the nitrogen remains behind.

The oxygen can be removed from atmospheric air also by certain metals at an elevated temperature. Thus, when metallic copper is heated to redness in the presence of atmospheric air, the oxygen combines with the copper, forming cupric oxide, CuO, and the nitrogen remains behind.

To prepare nitrogen of a high degree of purity, certain chemical reactions are made use of. When ammonium nitrite, a compound having the composition NH_4NO_2, is heated, the following reaction takes place: —

$$NH_4NO_2 = 2\,H_2O + N_2.$$

This is an excellent method for preparing pure nitrogen.

Properties of Nitrogen. — Nitrogen is characterized by its inertness, not only at ordinary temperatures, but even at elevated temperatures. On account of its chemical inactivity nitrogen cannot support combustion.

It cannot support life, all animals dying in a very short time when compelled to breathe only nitrogen. Nitrogen is a tasteless, odorless, colorless gas. It forms a colorless liquid, boiling at $-196°$. One litre of nitrogen weighs 1.2521 grams. When liquid nitrogen is cooled to $-214°$, it solidifies.

COMPOUND OF NITROGEN WITH HYDROGEN

Ammonia, NH_3. — The best-known compound of nitrogen and hydrogen is ammonia. Ammonia occurs in nature in small quantities in the free condition. In the form of its salts it occurs in many soils, and on account of their great solubility the salts of ammonia exist largely in solution in water. The ammonia is liberated in considerable quantity by decomposing organic matter. This is readily detected by the odor of the gas escaping from decomposing animal remains or decaying vegetable matter.

Ammonia can be formed by the direct union of hydrogen and nitrogen. When one part of nitrogen is mixed with three parts of hydrogen and electric sparks passed through the mixture, a part of the hydrogen and nitrogen combine, forming ammonia: —

$$N_2 + 3\,H_2 = 2\,NH_3.$$

The volume of the ammonia formed is just half the sum of the volumes of the nitrogen and hydrogen which have disappeared. *When one volume of nitrogen combines with three volumes of hydrogen, there are two volumes of ammonia formed.*

This shows again the simple relations by volume in which gases combine, and the simple relation between the volumes of the original gases and the volume of the product.

Ammonia is most conveniently prepared by the action of a base on an ammonium salt. When ammonium chloride is boiled with an aqueous solution of a strong base like sodium hydroxide, ammonia gas is liberated: —

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3.$$

In the laboratory ammonia is prepared most conveniently by mixing slaked lime with ammonium chloride, and warming the mixture. The reaction is —

$$2\,NH_4Cl + Ca(OH)_2 = CaCl_2 + 2\,H_2O + 2\,NH_3.$$

Ammonia was formerly obtained from decaying organic matter, and from ammonium salts which occurred in certain arid regions of the earth. The ammonium chloride which occurred in the neighborhood of the temple of Jupiter Ammon was termed *sal ammoniac*, whence the origin of the name ammonia. Ammonia to-day is obtained mainly by the dry distillation of coal in the manufacture of illuminating gas.

Chemical Properties of Ammonia. — Ammonia in the pure, dry condition is not active chemically. *When perfectly dry ammonia gas is brought in contact with perfectly dry hydrochloric acid gas, there is not the slightest reaction between the two substances.* If there is a mere trace of moisture present, the two gases react at once, forming the solid ammonium chloride.

Ammonia dissolves in water with the greatest ease, forming a compound which neutralizes acids and which is, therefore, *a basic substance.*

When ammonia dissolves in water, it combines with the water, forming the compound NH_4OH: —

$$NH_3 + H_2O = NH_4OH.$$

The compound NH_4OH which, however, has never been isolated, is then acted on by more water, and dissociates thus: —

$$NH_4OH = \overset{+}{N}H_4, \overset{-}{O}H.$$

The hypothetical group NH_4 is called ammonium. While this group has not been isolated, there is little doubt as to its existence. It plays the same rôle, as we shall see, that a metal atom does in the formation of compounds.

Physical Properties of Ammonia. — Ammonia is a colorless gas with a very penetrating odor. One litre of ammonia at 0° and 760 mm. pressure weighs 0.775 grams.

Liquid ammonia has *a very high specific heat*, which is the same as to say that a large amount of heat is required to produce a small rise in temperature. According to some authorities, slightly higher even than water. On account of its high specific heat and high heat of vaporization it is an excellent refriger-

ating agent, and is used extensively for this purpose, especially in connection with the *artificial preparation of ice.* Ammonia gas is liquefied by pressure, a large amount of heat being, of course, set free during the process. This heat is removed by a current of cold water flowing around the vessel in which the liquefaction is taking place. The liquid ammonia then flows into tubes which closely surround the vessels containing the water which is to be frozen, and is allowed to vaporize in these tubes. In vaporizing it must obtain heat from somewhere, and takes it from surrounding objects. The water loses its heat, is cooled below the freezing temperature and solidifies. The ammonia, having passed into the form of vapor, is not lost, but is pumped into the liquefying chamber, subjected again to pressure and liquefied, the heat set free being again removed by the current of cold water. The process is thus a continuous one, the same ammonia being used over and over again.

Machines for freezing water by means of liquid ammonia were early devised by Carré and are known as *Carré ice machines.* Many of the modern devices are modifications of these machines of Carré, utilizing exactly the same principles.

A few years ago most of the "artificial ice" was made by the ammonia process. Now, considerable ice is obtained by allowing water to evaporate into a space under diminished pressure.

Ammonium Amalgam, NH_4Hg. — While the compound NH_4 has never been isolated, its amalgam, or compound with mercury, is readily prepared. When sodium amalgam, a compound of sodium and mercury having the composition NaHg, is treated with a concentrated solution of ammonium chloride, the amalgam swells up, occupying a relatively large volume. The product has a metallic lustre, and is probably ammonium amalgam. The reaction probably takes place in the sense of the following equation: —

$$NaHg + NH_4Cl = NaCl + NH_4Hg.$$

It would seem that ammonium amalgam was a hopeful substance from which to obtain the group ammonium. It is, however, unstable, breaking down at ordinary temperatures into ammonia, hydrogen, and mercury.

COMPOUNDS OF NITROGEN WITH OXYGEN AND HYDROGEN

Ammonium Hydroxide, NH_4OH. — We have already seen that ammonium hydroxide is a basic substance. This is a compound of nitrogen with oxygen and hydrogen, and must be considered here. The most characteristic property of this substance is its basic nature. Being a base, it neutralizes acids forming salts. Ammonium hydroxide unites readily with hydrochloric acid, forming the well-characterized, beautifully white salt, ammonium chloride: —

$$\overset{+}{N}H_4, \overset{-}{O}H + \overset{+}{H}, \overset{-}{Cl} = H_2O + \overset{+}{N}H_4, \overset{-}{Cl}.$$

As the water is removed, the ammonium and chlorine ions combine, forming ammonium chloride: —

$$\overset{+}{N}H_4, \overset{-}{Cl} = NH_4Cl.$$

Compounds of Nitrogen with Oxygen. — Nitrogen forms the following compounds with oxygen: Nitrous oxide, N_2O; nitric oxide, NO; nitrogen sesquioxide or trioxide, N_2O_3; nitrogen dioxide or tetroxide, depending upon whether it has the composition NO_2 or N_2O_4; and nitrogen pentoxide, N_2O_5.

We shall now study these compounds in some detail.

Nitrous Oxide, N_2O. — Nitrous oxide is formed when ammonium nitrate is heated to 250°. The following equation expresses the reaction that takes place: —

$$NH_4NO_3 = 2\,H_2O + N_2O.$$

The oxygen and hydrogen combine and form water, and the nitrogen and oxygen form the compound N_2O, which escapes.

Nitrous oxide is a remarkable substance, in that it supports combustion almost as well as pure oxygen. Phosphorus and carbon burn readily in nitrous oxide. Certain substances, however, burn in oxygen and burn, but not so readily, in nitrous oxide. The products of combustion in nitrous oxide are the same as in pure oxygen, showing that the compound N_2O is readily broken down, yielding free oxygen.

When nitrous oxide is inhaled into the lungs, it produces a remarkable physiological effect, generally throwing the subject into a hysterical condition. It is, therefore, known as *laughing gas*. When consumed in larger quantity it produces anesthesia, and is consequently used in minor surgical operations.

Nitrous oxide is a colorless gas, with a sweetish taste, and dissolves readily in cold water. It should, therefore, be collected in cylinders over hot water.

When most chemical reactions take place, heat is evolved, — most reactions are *exothermic*. In this case the opposite is true. When nitrogen and oxygen combine to form nitrous oxide, heat is absorbed. Such chemical reactions, which take place with absorption of heat, are known as *endothermic reactions*.

Nitric Oxide, NO. — Nitric oxide can be formed by the reduction of the higher oxides of nitrogen or by the reduction of nitrous or nitric acid. It is prepared most conveniently by the action of nitric acid on metallic copper. The equations expressing the reaction are: —

$$3\,Cu + 2\,HNO_3 = 3\,CuO + H_2O + 2\,NO;$$
$$3\,CuO + 6\,HNO_3 = 3\,Cu(NO_3)_2 + 3\,H_2O.$$

As quickly as the colorless gas, nitrous oxide, is brought in contact with free oxygen, the two combine at ordinary temperature: —

$$2\,NO + O_2 = 2\,NO_2.$$

The gas NO_2 has a yellowish brown color. These are the fumes which always appear when nitric acid acts on metallic copper. Nitric oxide produces a dark violet color when

brought in contact with a solution of a ferrous salt. This reaction is used to detect nitric oxide.

Nitrogen Sesquioxide or Nitrogen Trioxide, N_2O_3. — Nitrogen sesquioxide is obtained by the action of arsenic trioxide, As_2O_3, upon nitric acid. Also by the action of a strong acid, like sulphuric, upon nitrites: —

$$2\,NaNO_2 + H_2SO_4 = Na_2SO_4 + H_2O + N_2O_3.$$

It is, therefore, sometimes called nitrous anhydride, since it is nitrous acid minus water, and, by the addition of an alkali, it forms nitrites. Nitrogen sesquioxide is stable only at low temperatures. Above $-20°$, or $-15°$, it begins to decompose into nitrogen dioxide and nitric oxide: —

$$N_2O_3 = NO_2 + NO.$$

At very low temperatures it passes over into a deep blue liquid.

Nitrogen Dioxide or Nitrogen Peroxide, NO_2. — Nitrogen dioxide is conveniently formed by the action of oxygen on nitric oxide: —

$$2\,NO + O_2 = 2\,NO_2.$$

Nitrogen peroxide is a strong oxidizing agent. It is also very poisonous.

Nitrogen Pentoxide, N_2O_5. — Nitrogen pentoxide is formed by the action of strong dehydrating agents, like phosphorus pentoxide, upon nitric acid: —

$$2\,HNO_3 + P_2O_5 = (P_2O_5.H_2O) + N_2O_5.$$

Nitrogen pentoxide readily combines with water, forming nitric acid: —

$$N_2O_5 + H_2O = 2\,HNO_3.$$

It is, therefore, the anhydride of nitric acid. It is a powerful oxidizing agent, as would be expected from the large amount of oxygen which it contains.

Nitrous Acid, HNO_2. — The salts of nitrous acid, the nitrites, are obtained by removing oxygen from the nitrates.

If a mild reducing agent, such as metallic lead, is fused with a nitrate, the reduction to nitrite takes place far more easily and completely: —

$$KNO_3 + Pb = PbO + KNO_2.$$

When a nitrite is treated with a strong acid, such as sulphuric, nitrous acid is set free: —

$$2\,KNO_2 + H_2SO_4 = K_2SO_4 + 2\,HNO_2.$$

Nitrous acid can exist only in solution. When an attempt is made to remove the water, the nitrous acid loses water and passes into the anhydride, N_2O_3: —

$$2\,HNO_2 = H_2O + N_2O_3.$$

Nitrous acid is an excellent reducing agent, since it readily combines with oxygen, forming nitric acid. When brought in contact with a substance rich in oxygen, like potassium permanganate, it takes oxygen away from the compound, converting it into colorless substances. The destruction of the beautiful purple color takes place very rapidly.

Nitric Acid, HNO_3. — This is not only the most important acid of nitrogen, but one of the strongest and most important of all known acids. It was early prepared from nitre, which is potassium nitrate, whence its name.

$$H_2SO_4 + 2\,KNO_3 = K_2SO_4 + 2\,HNO_3.$$

Potassium nitrate, known as saltpetre, is formed where organic matter is decomposing in the presence of potassium salts. It occurs in the form of a solid only in arid regions, since, on account of its great solubility, it would pass into solution if it came in contact with any appreciable amount of water. Sodium nitrate occurs in abundance in the arid regions of Chili, and is known as Chili saltpetre. When sodium nitrate is treated with sulphuric acid, the first reaction that takes place is: —

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

If the temperature is raised sufficiently, the acid sulphate acts on more of the nitrate, decomposing it in the sense of the following equation: —

$$NaHSO_4 + NaNO_3 = Na_2SO_4 + HNO_3.$$

The decomposition of nitrates by sulphuric acid does not mean that sulphuric acid is stronger than nitric acid. The nitric acid being volatile is set free, although it is much stronger than sulphuric acid.

Chemical Properties of Nitric Acid. — The most characteristic chemical property of nitric acid is its strong oxidizing power. When brought in contact with substances which can take up oxygen, nitric acid readily gives up its oxygen and passes over into lower oxides of nitrogen.

The oxidizing action of nitric acid and its salts can be represented as follows: —

$$4\,HNO_3 = 2\,H_2O + 4\,NO_2 + O_2;$$
$$4\,HNO_3 = 2\,H_2O + 4\,NO + 3\,O_2;$$
$$4\,HNO_3 = 2\,H_2O + 2\,N_2 + 5\,O_2;$$

the reaction that takes place in any given case depending upon the nature of the substance present and upon the conditions.

When a metal is treated with nitric acid, the hydrogen ion of the acid gives up its charge to the metal, converting the latter into an ion, while the hydrogen becomes an atom. The hydrogen, in the case of nitric acid, however, does not escape, but acts on more nitric acid, reducing it to lower oxides of nitrogen, or to nitrogen itself, or even to ammonia, depending upon conditions.

Nitric acid is a liquid, boiling with partial decomposition at 86°.

Nitric acid and water are miscible in all proportions.

Detection of Nitric Acid. — Nitric acid is readily detected by the dark purple color produced when it is mixed with a concentrated solution of ferrous sulphate, both solutions being warm. The test for nitric acid is made as follows: The

nitric acid or the nitrate is treated with a little concentrated sulphuric acid, and warmed until the containing vessel feels warm to the hand. Another test-tube is filled about one-third full of crystals of ferrous sulphate, and dissolved in just as little water as possible, the solution being heated until it feels warm to the hand, but not heated to boiling. The solution containing the nitric acid is now added drop by drop to the solution of ferrous sulphate, when the dark color will make its appearance in the form of a ring where the two liquids come in contact.

Dissociation of Nitric Acid and Nitrates. — Nitric acid dissociates in the sense of the following equation: —

$$HNO_3 = \overset{+}{H},\ \overset{-}{NO_3}.$$

It is, therefore, a monobasic acid, and can yield only one series of salts. These are of the general type, MNO_3, and dissociate thus: —

$$MNO_3 = \overset{+}{M},\ \overset{-}{NO_3}.$$

Fuming Nitric Acid. — Fuming nitric acid is formed in the preparation of nitric acid from sodium nitrate and sulphuric acid, if the temperature is sufficiently high. It is apparently a solution of nitrogen dioxide in nitric acid.

It is a much more energetic oxidizing agent than ordinary concentrated nitric acid. When warmed in its fumes many organic substances take fire and burn.

Aqua Regia. — Certain metals, like gold and platinum, do not dissolve in nitric acid, but when treated with a mixture of nitric and hydrochloric acids they dissolve readily. The mixture which is most efficient consists of one part of nitric acid and three parts of hydrochloric acid. This is known as *aqua regia*. The nitric acid in the mixture oxidizes the hydrochloric acid and liberates chlorine. There is probably also formed one or more compounds containing nitrogen, oxygen, and chlorine.

The action of these various substances is to convert the

metals into chlorides, even platinum being transformed into platinic chloride by aqua regia. The name was derived from the fact that this mixture can dissolve gold.

EXPERIMENTS WITH NITROGEN AND ITS COMPOUNDS WITH HYDROGEN AND OXYGEN

Experiment 38. Nitrogen obtained from the Air. — (Bell-jar closed by a cork; pneumatic trough filled with water; small porcelain dish; a piece of phosphorus the size of a pea.)

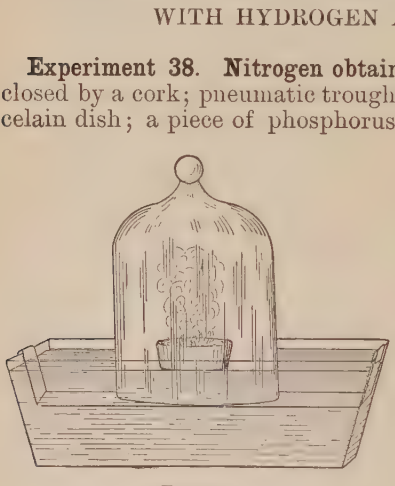

FIG. 24.

Arrange the apparatus as shown in Figure 24. A small piece of phosphorus, *not larger than a pea,* is dried by pressing it between folds of filter-paper. Phosphorus must never be touched with the hand, or painful wounds may result from the ignition of the phosphorus. The phosphorus is placed in the porcelain dish, which is floated upon water as in the figure. The phosphorus is ignited, and the bell-jar placed over it on the shelf in the trough, so that it dips well beneath the surface of the water. As the phosphorus burns the air in the bell-jar becomes heated, and some may escape in the form of bubbles from the bottom of the jar. After the phosphorus has ceased to burn, the water will rise in the bell-jar.

Examine the gas which remains in the jar to see whether it is nitrogen. After bringing the water inside the jar to the same level as that outside, by raising or lowering the jar in the trough, remove the cork and introduce quickly a burning taper, or a burning piece of sulphur, and observe what happens. Nitrogen will not support combustion. Do these results indicate the presence of nitrogen? (See page 76.)

Experiment 39. Preparation of Nitrogen from Ammonium Nitrite. — (Flask holding 250 to 300 cc.; thistle-tube; two-hole stopper; exit-tube; ammonium chloride; sodium nitrite.)

Introduce into the flask (Fig. 25) 15 grams of ammonium chloride and 20 grams of sodium nitrite. Pour in 50 cc. of water. Heat the flask slowly. Nitrogen will be evolved before there is any boiling in the flask. When ammonium chloride is heated in such a solution with sodium nitrite, ammonium nitrite is formed in sense of the following equation: —

$$NH_4Cl + NaNO_2 = NaCl + NH_4NO_2.$$

The ammonium nitrite then decomposes in the manner already described.

Test the gas as in the last experiment. Does it support combustion? (See page 76.)

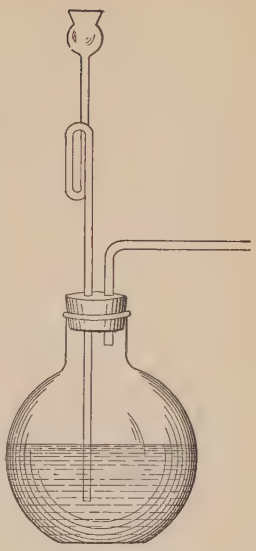

Fig. 25.

Experiment 40. Preparation of Ammonia from Ammonium Chloride and Sodium Hydroxide. — (Test-tube; ammonium chloride; sodium hydroxide.)

Introduce into a test-tube enough ammonium chloride to make a layer about 1 cm. deep. Add a few drops of a concentrated solution of sodium hydroxide. Notice the odor of the gas that escapes. Warm the tube gently and notice that the odor becomes more intense. Moisten a piece of red litmus paper and observe the change in color. This is a characteristic reaction of alkalies in general. (See page 77.)

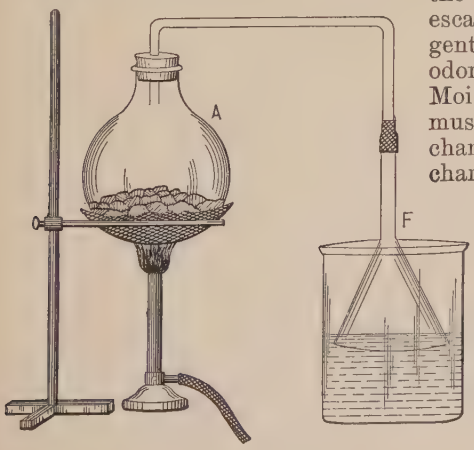

Fig. 26.

Experiment 41. Preparation of Ammonia from Ammonium Chloride and Slaked Lime. — (Flask holding 500 cc.; stopper; delivery-tube; funnel; beaker.)

Arrange the apparatus as shown in Figure 26. Into the flask *A* introduce 150 grams of dry slaked lime mixed with 100 grams of ammonium chloride. Place the flask upon a sand-bath or an asbestos board and heat gently. Ammonia gas will escape. Collect some of the gas in water by attaching a funnel *F* to the delivery-tube as in the figure and as in Figure 23. The funnel must dip only a short distance beneath the surface of the water. Ammonia is very soluble in water, and if this precaution is not taken the water will absorb the ammonia very rapidly and rush back into the flask *A*. This solution, known as ammonia water, should be preserved for future experiments.

Collect some of the ammonia in cylinders by attaching the tube *T* (Fig. 27) to the delivery-tube from the flask *A* (Fig. 26). The tube *T* must extend to the top of the inverted cylinder, since ammonia is lighter than air. The ammonia then displaces the air and the cylinder can be readily filled with the gas. (See page 77.)

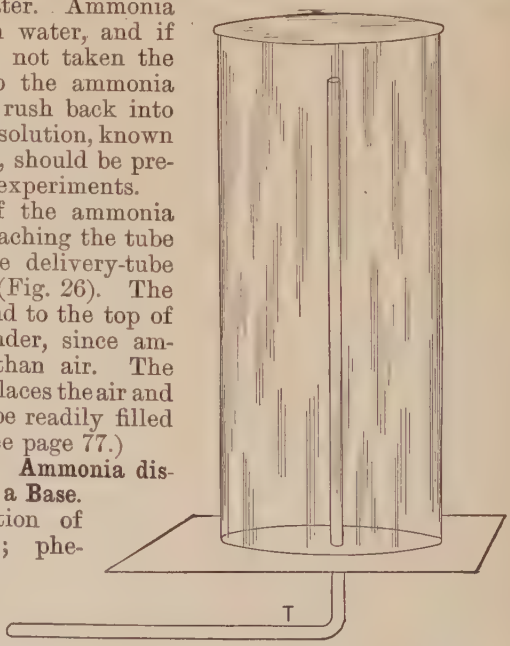

Fig. 27.

Experiment 42. Ammonia dissolved in Water is a Base. — (Aqueous solution of ammonia; litmus; phenolphthaleïn.)

To a portion of the solution of ammonia in water obtained in Experiment 41, add a few drops of litmus. Litmus in the presence of a neutral substance is purple. In the presence of aqueous ammonia it is deep blue in color. This reaction is characteristic of alkalies in general.

To another portion of the aqueous solution of ammonia add a few drops of the alcoholic solution of phenolphthaleïn. The solution becomes deep red in color. This reaction is also characteristic of alkalies. This color may disappear in the case of ammonia after a time. (See page 78.)

Experiment 43. Neutralization of Ammonia by Acids. — (Three beakers; aqueous solution of ammonia; dilute hydrochloric acid; dilute sulphuric acid; dilute nitric acid.)

Introduce 50 cc. of distilled water into each beaker and add 25 cc. of the solution of ammonia to each. Also a few drops of litmus.

Into one beaker drop from a pipette dilute hydrochloric acid, stirring the solution vigorously by means of a stirring rod each time a drop of the acid falls into the solution of ammonia. After a time the solution will turn red, showing that all the ammonia has been neutralized.

Add sulphuric acid in the same manner to the second beaker, and nitric acid to the third until the litmus turns red in each case. Preserve the solutions. (See page 80.)

Experiment 44. A Salt is formed when Ammonia is Neutralized by an Acid. — (~~Three~~ small evaporating dishes; the three solutions obtained in the last experiment.)

Pour the three solutions obtained in the last experiment into the three evaporating dishes — one in each dish. Evaporate the solutions to dryness. A white salt will remain in each dish — ammonium chloride in one dish, ammonium sulphate in another dish, and ammonium nitrate in the third.

Introduce some of the ammonium chloride into a test-tube, some of the ammonium sulphate into a second test-tube, and some of the ammonium nitrate into a third test-tube. Add a few drops of caustic soda to each tube and warm gently. Notice the odor of ammonia escaping from each tube. Test for ammonia with red litmus paper. This reaction is characteristic of ammonium salts. (See page 80.)

Experiment 45. Gaseous Ammonia reacts with Gaseous Hydrochloric Acid. — (Cylinder filled with ammonia; two glass plates; cylinder containing a few drops of concentrated hydrochloric acid.)

Introduce a few drops of concentrated hydrochloric acid into a glass cylinder and cover the top of the cylinder with a glass plate. Place above this a cylinder filled with ammonia gas also covered with a glass plate. The apparatus should be arranged as in Figure 13. Remove the plates, bringing the two cylinders together. The gases combine at once, forming ammonium chloride, which is deposited upon the walls as a white powder. Collect a little of the powder, place it in a test-tube, and add a few drops of sodium hydroxide. Notice the odor of ammonia. This characteristic reaction of ammonium

salts shows that a salt of ammonium was formed in the above reaction. (See page 78.)

Experiment 46. Ammonia Lighter than Air. — (Large balance (Fig. 2); two large beakers; large bottle filled with ammonia.)

Remove the glass cylinders from the large balance (Fig. 2), and suspend a large beaker from each arm of the balance. When equilibrium has been established and the pointer made to stand at zero by adding weights to one or the other arm, the bottle of ammonia is opened beneath one of the beakers. This arm of the balance will be seen to rise at once, showing that ammonia is lighter than air. (See page 78.)

Experiment 47. Absorption of Ammonia by Water. — (Large glass tube about 30 cm. in length closed at one end; iron stand and clamp; mercury trough.)

Fill the glass tube (Fig. 28) with mercury and insert it into the mercury trough, which also contains considerable mercury. Fill the tube with ammonia by leading the discharge tube from the ammonia-generating apparatus beneath the lower end of the glass tube. As the ammonia rises in the glass tube, the mercury will be displaced and will flow out into the mercury trough.

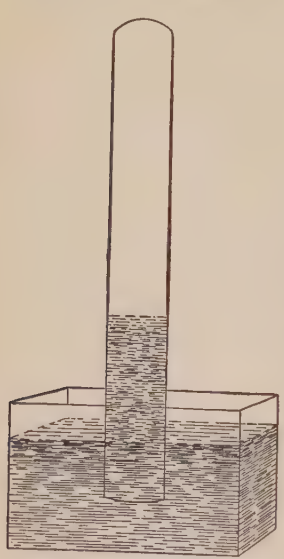

Fig. 28.

When the glass tube has become filled with ammonia gas, add a few drops of water to the tube by means of a bent glass tube filled with water and placed beneath the lower end of the tube containing ammonia. The water will rise to the top of the mercury in the tube, absorb the ammonia, and the mercury will rise in the tube as the ammonia is absorbed. (See page 78.)

Experiment 48. Absorption of Ammonia by Water. — (Two large balloon flasks; glass tubing; one one-hole rubber stopper; one two-hole rubber stopper; iron stand and clamp.)

The apparatus is to be arranged as in Figure 29. The balloon flask *B*, holding about 2 litres, is cleaned and dried and filled

with ammonia by inverting the flask and passing the escape-tube from the ammonia-generating flask up to the top of the inverted flask. Ammonia being lighter than air drives the air downwards out of the flask and completely fills it. The lower flask *A*, holding 3 litres, is filled with distilled water containing a little litmus, to which just enough acid is added to color the litmus red.

The apparatus is now arranged as shown in the figure. The breath is then blown into the tube *C*. This forces a little water from the flask *A*, through the tube *D*, into the flask *B*. The water which enters *B* absorbs the ammonia, producing a partial vacuum in *B*. Water immediately rushes up from *A* into *B*, and a fountain results. The ammonia in *A* first neutralizes the acid in the water and then renders the water alkaline, changing the color of the litmus from red to blue.

If the precaution was taken to completely fill the flask *B* with ammonia, *i.e.* to pass in the ammonia until all the air had been displaced, water will rise in *B* until this flask is practically full.

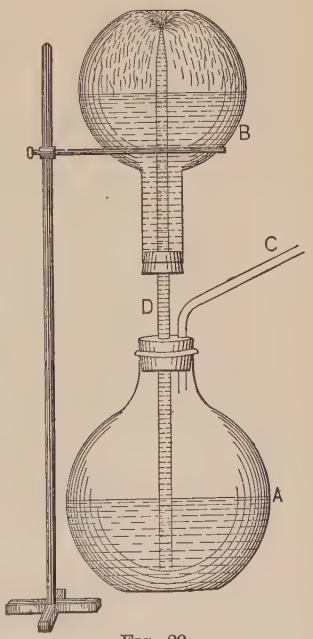

FIG. 29.

The iron stand and clamp must be so firm as to hold the flask *B* when full of water. (See page 78.)

Experiment 49. Absorption of Ammonia by Charcoal. — (Glass tube filled with ammonia; mercury trough; a piece of charcoal which has been freshly heated.)

Fill a glass tube with ammonia, as in Figure 28. Introduce a piece of freshly heated charcoal by pushing it under the mercury beneath the mouth of the tube, and allowing it to rise in the tube. The charcoal will absorb the ammonia and the mercury will rise in the tube.

This illustrates the way in which charcoal absorbs ammonia and other gases from water and thus purifies it.

Experiment 50. Preparation of Nitrous Oxide. — (Retort holding about 100 cc.; pneumatic trough; glass cylinders with glass plates as covers; ammonium nitrate.)

Introduce 15 grams of ammonium nitrate, which had been previously dried at 110° in an air-bath to remove moisture, into the retort arranged as in Figure 3. Heat the retort very gently; indeed, just rapidly enough to obtain a steady current of gas. Rapid heating may produce frothing in the retort, or even explosion.

It is better to have the water in the trough somewhat warm, since nitrous oxide is less soluble in warm water than in cold.

Fill several cylinders with the gas for use in the next experiment. (See page 80.)

Experiment 51. Nitrous Oxide supports Combustion. — (Four or five cylinders filled with nitrous oxide; deflagrating-spoon; a splinter; sulphur; phosphorus; steel watch-spring.)

Into one of the cylinders introduce a splinter which has been burned at the end to a coal, but from which the flame has been extinguished. It will be rekindled into flame.

Into another cylinder introduce highly heated, burning sulphur in a deflagrating-spoon, and into still another cylinder introduce burning phosphorus. They will burn with intense light and with the evolution of a large amount of heat, as in oxygen.

Cover the bottom of the fourth cylinder, filled with nitrous oxide, with a sheet of asbestos and a layer of water, and plunge into the cylinder a steel watch-spring tipped with sulphur and ignited. The iron will burn very vigorously, sending off brilliant scintillations. The asbestos and water were introduced into the cylinder so that the molten metal and oxide would not fall on to the bottom of the cylinder and break it.

In all of the above experiments the products of combustion are the same as in oxygen, and, therefore, they suggest combustion in oxygen in a most striking manner. (See page 81.)

Experiment 52. Preparation of Nitric Oxide. — (A balloon flask, or Florence flask, holding 500 cc.; a thistle-tube; a delivery-tube bent at right angles; a two-hole stopper; copper turnings; concentrated nitric acid.)

Into the balloon flask (Fig. 30) introduce some copper turnings and pour slowly on to the turnings concentrated nitric acid. When a steady stream of the gas is evolved cease to add the nitric acid, since an excess of acid frequently produces frothing in the flask.

The gas which first escapes is reddish brown in color, due to the combination of nitric oxide with the oxygen of the air in the flask, forming nitric oxide.

After the gas in the flask has become practically colorless, fill several cylinders in a pneumatic trough over water. The gas in the cylinders will be seen to have very little color. (See page 81.)

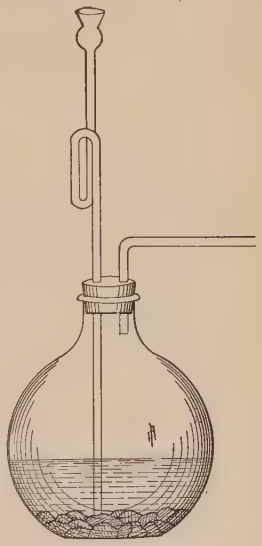

Fig. 30.

Experiment 53. Combination of Nitric Oxide with Oxygen. — (Glass cylinder filled with nitric oxide, covered with a glass plate; glass cylinder filled with air.)

Arrange the apparatus as in Figure 13; remove the glass plates between the two cylinders and allow the nitric oxide to come in contact with the air. Dense red fumes will appear immediately on bringing the two gases in contact. Observe carefully the movements of the red vapor in the cylinder. (See page 81.)

Experiment 54. Nitric Oxide does not support Combustion. — (Three or four cylinders filled with nitric oxide; a splinter; a piece of charcoal; a piece of sulphur.)

Into a cylinder filled with nitric oxide introduce a burning splinter; observe what occurs.

Into another cylinder filled with nitric oxide introduce a piece of sulphur ignited in a deflagrating-spoon. Does it continue to burn?

Into a third cylinder filled with the gas introduce a piece of carbon heated to redness. Does the carbon continue to burn?

Compare these results with those obtained with nitrous oxide.

Experiment 55. Preparation of the Anhydride of Nitrous Acid; Nitrogen Sesquioxide. — (Balloon or Florence flask holding 200 to 300 cc.; thistle-tube; two-hole stopper; delivery-tube bent at right angles; small cylinder; large bottle or cylinder; a U-tube surrounded by ice and salt; arsenic trioxide; nitric acid of the specific gravity 1.35.)

Thirty grams of arsenic trioxide are introduced into the flask *A* (Fig. 31). This is covered with nitric acid of the

specific gravity 1.35, and gently warmed. The heavy red gas nitrogen trioxide, can be collected in a bottle or cylinde by leading the exit-tube to the bottom of the vessel place upright.

If the gas is passed through the U-tube (Fig. 31) surrounde by ice and salt, it condenses, forming a blue liquid. The gas i first passed through the bottle *B* in order that any steam may condense. (See page 82.)

Experiment 56. Preparation of Nitrogen Peroxide — (Balloon or Florence flash holding 250 cc.; two hole rubber stopper; thistle-tube; discharge-tube U-tube; tin; concentrated nitric acid; ice; salt.)

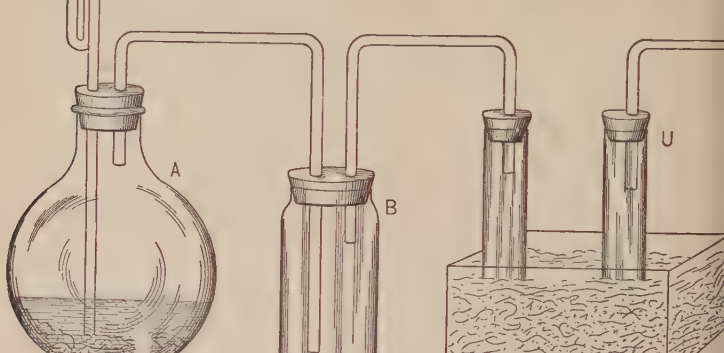

Fig. 31.

Introduce into the flask some granulated tin, and cover this with concentrated nitric acid. The gas may be passed through an empty flask to allow the steam to condense, and then through the U-tube surrounded by ice and salt as in Figure 31. The gas is liquefied in the U-tube, forming a reddish liquid.

Compare this with the liquid obtained in Experiment 55. (See page 82.)

Experiment 57. Preparation of Nitric Acid. — (Tubulated retort holding from 300 to 500 cc.; receiver; large funnel; sodium nitrate; concentrated sulphuric acid.)

Arrange the apparatus as in Figure 32. Introduce into the retort 50 grams of sodium nitrate, and add 25 grams of concentrated sulphuric acid. Warm gently the contents of the

retort. Nitric acid will condense in the receiver, which is kept cool by a current of water which flows over the outside of the receiver. Nitric acid prepared in this way is colored somewhat yellow, due to the presence of oxides of nitrogen dissolved in it. With nitric acid perform the following experiments. (See page 83.)

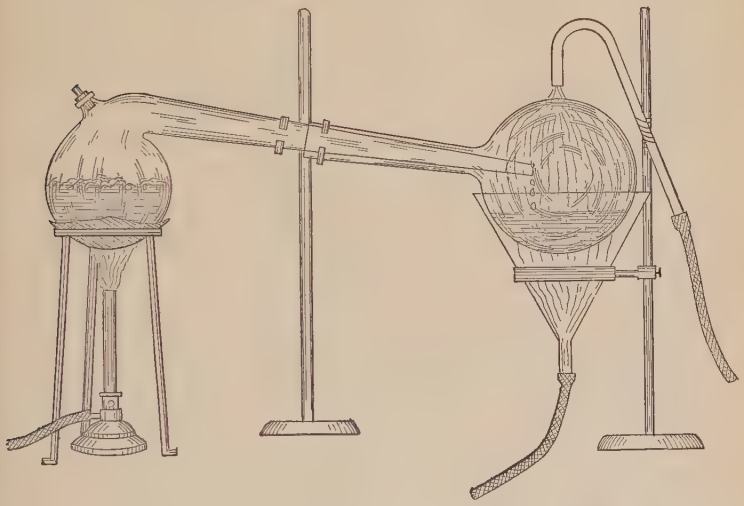

Fig. 32.

Experiment 58. Acid Properties of Nitric Acid. — (Nitric acid; sodium hydroxide; litmus.)

Dip a piece of blue litmus paper into a solution of a few drops of nitric acid in a large volume of water. Observe how quickly the blue litmus turns deep red in color — a characteristic reaction of acids.

Introduce 10 cc. of concentrated nitric acid into a beaker containing 50 cc. of distilled water; note the temperature; add a few drops of litmus. Add cautiously from a pipette potassium hydroxide, stirring the solution vigorously. As soon as the litmus changes from red to blue, cease to add the alkali. Note again the temperature of the solution. Has there been any change? Why?

Evaporate the solution to dryness; a white solid is obtained which is potassium nitrate. Save for future use. (See page 84.)

Experiment 59. Fuming Nitric Acid. — (Tubulated retort holding 300 cc. to 500 cc.; receiver; concentrated nitric acid, concentrated sulphuric acid.)

This experiment is to be performed only by the instructor. Arrange the apparatus as in Figure 32. Pour cautiously 150 grams of concentrated sulphuric acid into 75 grams of concentrated nitric acid. Introduce the mixture into the retort, and distil *slowly* under the hood. The nitric acid which condenses and is caught in the receiver is known as fuming nitric acid. The sulphuric acid has taken up a part of the water present, and the nitric acid which distils over is much stronger than ordinary concentrated nitric acid. (See page 85.)

Experiment 60. Oxidizing Power of Nitric Acid. — (*Action on sugar.*) (Nitric acid; Erlenmeyer flask 100 cc.; cane sugar.)

Introduce 5 grams of cane sugar into the Erlenmeyer flask, and add 20 cc. of concentrated nitric acid. Little or no reaction takes place. Warm the mixture. A violent reaction will take place, resulting in the evolution of large volumes of dense red fumes. The sugar is oxidized by the hot nitric acid. Evaporate the solution until only a small volume remains. Set this aside in a beaker or crystallizing dish, and beautiful white crystals will separate. These are crystals of oxalic acid. (See page 84.)

Experiment 61. Oxidizing Power of Nitric Acid. — (*Action on wood and charcoal.*) (An Erlenmeyer flask 100 cc.; beaker holding 200 cc.; fuming nitric acid; splinter; stick of charcoal.)

Introduce 25 cc. of the acid into the Erlenmeyer flask and heat. Plunge a glowing splinter into the liquid. It will burn vigorously.

Pour 50 cc. of fuming nitric acid into the beaker. Heat one end of the stick of charcoal to redness, holding the stick with a pair of forceps. Quickly plunge the hot end into the nitric acid. The charcoal will continue to burn under the liquid. Where does the oxygen which combines with the carbon come from?

This experiment must be performed under the hood on account of the escape of noxious vapors. (See page 84.)

Experiment 62. Oxidizing Power of Nitric Acid. — (*Action on tin.*) (Erlenmeyer flask; concentrated nitric acid; some granules of tin.)

Into a small Erlenmeyer flask introduce a few granules of tin; cover these with concentrated nitric acid and warm cautiously. Red fumes will escape, and the tin will disappear.

It will, however, not pass into solution, but a white powder will be formed. This is an oxide of tin.

From what source did the tin obtain the oxygen? (See page 84.)

Experiment 63. Nitric Acid dissolves Certain Metals. — (Erlenmeyer flask 100 cc.; granules of zinc; nitric acid.)

Into the Erlenmeyer flask introduce some pieces of zinc and cover the zinc with nitric acid. The zinc rapidly passes into solution. What escapes? Evaporate the solution to dryness. White zinc nitrate separates. (See page 84.)

Experiment 64. Action of Nitric Acid on Hydrochloric Acid (*Aqua Regia*). — (Large test-tube; concentrated nitric acid; concentrated hydrochloric acid.)

Mix 10 cc. of concentrated nitric acid and 30 cc. of concentrated hydrochloric acid, and fill the test-tube one-third full of the mixture. Warm gently over a bunsen burner. A gas will escape whose odor suggests that of chlorine. It contains in addition to chlorine certain oxides of nitrogen and chlorine.

The nitric acid oxidizes the hydrochloric acid.

This mixture readily dissolves gold and even platinum. (See page 85.)

Experiment 65. Detection of Nitric Acid. — (Two test-tubes; nitric acid; a nitrate; concentrated sulphuric acid; ferrous sulphate.)

Into one test-tube introduce the nitric acid or the nitrate, and some concentrated sulphuric acid. Warm until the tube feels warm to the hand.

Fill the other test-tube about one-third full with crystals of green ferrous sulphate. Add just enough water to cover the crystals and warm until the tube feels warm to the hand.

Slant both tubes and carefully pour a few drops from one into the other. Where the two solutions come in contact a dark purplish ring will be formed. This is the general test for nitric acid. (See page 84.)

CHAPTER X

NEUTRALIZATION OF ACIDS AND BASES

Bases are Hydroxyl Compounds. — Ammonium hydroxide when dissolved in water dissociates into the cation ammonium, and the anion hydroxyl. The hydroxyl ion and not the ammonium ion gives the characteristic basic property to the solution. This is shown by the fact that there are many compounds which, when dissolved in water, dissociate, yielding the ammonium ion, and these solutions have no basic properties. On the other hand, every compound which yields hydroxyl ions is a basic substance. That the statement that bases are hydroxyl compounds is correct can be seen at once by examining the composition of a number of basic substances: —

Sodium hydroxide	$NaOH$
Potassium hydroxide	KOH
Calcium hydroxide	$Ca(OH)_2$
Barium hydroxide	$Ba(OH)_2$
Aluminium hydroxide	$Al(OH)_3$

This list of basic substances could be greatly extended. It will be observed that they all contain a metal combined with one or more hydroxyl groups. When these substances dissociate, the hydroxyls split off as anions, and the metal forms the cation. A few examples will make this clear: —

$$NaOH = \overset{+}{Na}, OH.$$

$$KOH = \overset{+}{K}, \overset{-}{OH}.$$

$$Ca(OH)_2 = \overset{++}{Ca}, \overset{-}{OH}, \overset{-}{OH}.$$

$$Ba(OH)_2 = \overset{++}{Ba}, \overset{-}{OH}, \overset{-}{OH}.$$

$$Al(OH)_3 = \overset{+++}{Al}, \overset{-}{OH}, \overset{-}{OH}, \overset{-}{OH}.$$

Acidity of Bases and Basicity of Acids. — We observe in the above examples that some bases dissociate yielding one hydroxyl ion, other bases yield two hydroxyl ions, and others still, three hydroxyl ions. If we take a gram-molecular weight (the molecular weight of the substance in grams) of a monobasic acid and dissolve it in water, diluting the solution to a litre, and take a gram-molecular weight of any one of the above bases which yields one hydroxyl ion and dissolve it so as to form a litre of solution, the litre of the acid would exactly neutralize the litre of the base. Such a base which yields on dissociation one hydroxyl ion is known as a *monacid base*: —

$$\overset{+}{H},\ \overset{-}{Cl} + \overset{+}{Na},\ \overset{-}{OH} = H_2O + \overset{+}{Na},\ \overset{-}{Cl}.$$

If we prepare a solution of a base which dissociates into two hydroxyl ions, containing a gram-molecular weight in a litre, it will require just two litres of a solution of an acid such as that referred to above to neutralize the one litre of the base: —

$$\overset{++}{Ca},\ \overset{-}{OH},\ \overset{-}{OH} + \overset{+}{H},\ \overset{-}{Cl} + \overset{+}{H},\ \overset{-}{Cl} = 2\,H_2O + \overset{++}{Ca},\ \overset{-}{Cl},\ \overset{-}{Cl}.$$

Such bases are known as *diacid bases*. To neutralize a gram-molecular weight of a base which dissociates into three hydroxyl ions, requires just three litres of the above solution of acid. Such a base is termed a *triacid base*: —

$$\overset{+++}{Al},\ \overset{-}{OH},\ \overset{-}{OH},\ \overset{-}{OH},\ + \overset{+}{H},\ \overset{-}{Cl} + \overset{+}{H},\ \overset{-}{Cl} + \overset{+}{H},\ \overset{-}{Cl} =$$
$$3\,H_2O + \overset{+++}{Al},\ \overset{-}{Cl},\ \overset{-}{Cl},\ \overset{-}{Cl}.$$

Just as we have mono, di, and triacid bases, just so we have mono, di, and tribasic acids. An acid which dissociates, yielding one hydrogen ion, is *monobasic*: —

$$HCl = \overset{+}{H},\ \overset{-}{Cl}.$$

If the molecule of the acid yields two hydrogen ions, it is *dibasic*: —

$$H_2SO_4 = \overset{+}{H},\ \overset{+}{H},\ \overset{=}{SO_4}.$$

OF PHYSICAL EDUC

If the molecule of the acid dissociates, yielding three hydrogen ions, it is *tribasic:* —

$$H_3AsO_4 = \overset{+}{H},\ \overset{+}{H},\ \overset{+}{H},\ \overset{\equiv}{AsO_4};$$

and so on.

Salts. — When a dilute solution of an acid acts on a dilute solution of a base, what takes place and all that takes place is the formation of a molecule of water: —

$$\overset{-}{Cl},\ \overset{+}{H} + \overset{-}{OH},\ \overset{+}{Na} = H_2O + \overset{+}{Na},\ \overset{-}{Cl}.$$

The sodium ion remains after the process of neutralization in exactly the same condition as before, and, similarly, the chlorine remains in the ionic condition. The hydrogen and hydroxyl ions, however, unite and form a molecule of water. It is a general rule that, *whenever we have hydrogen and hydroxyl ions in the presence of one another uncombined, they unite and form water.* There is an abundance of direct experimental evidence in favor of this conclusion.

If, however, we evaporate the solution containing the sodium and chlorine ions, they unite and form a molecule of sodium chloride. This is a salt. We would define a salt as follows: *A salt is a compound formed by the union of an anion of an acid with a cation of a base.* This takes place generally, as already stated, only when the solution containing these ions is evaporated, and at least a part of the water removed.

The salts are named after the acids from which they are derived. Salts of hydrochloric acid are called *chlorides*, those of nitric acid *nitrates*, and those of sulphuric acid *sulphates.* In general, salts of acids which end in "*ic*" are termed "*ates.*" Salts of sulphurous acid are called sulphites, salts of nitrous acids nitrites, and so on. In general, the names of salts of acids which end in "*ous*," end in "*ite.*"

So much for the nomenclature of salts in terms of the acids. Since the cation also enters into the salt, we must be able to distinguish the salts of one cation from the salts of another cation. The name of the cation is used before the name of the

acid with whose salt we are dealing. Thus, the chloride of sodium is known as sodium chloride, the chloride of calcium, calcium chloride, and so on. When we come to a metal that shows different valence the case is a little more complicated.

Heat of Neutralization. — When solutions of acids and bases are brought together, heat is liberated. Quantitative measurements of the amounts of heat set free brought out a simple and very important relation. This can best be seen from the following results for strong acids and bases. Gram-molecular weights of different acids were brought together with a gram-molecular weight of a given base, both the acid and base being present in very dilute solution: —

	Heat of Neutralization
Hydrochloric acid and sodium hydroxide	13,700 cals.
Nitric acid and sodium hydroxide	13,700 cals.
Chloric acid and sodium hydroxide	13,760 cals.
Bromic acid and sodium hydroxide	13,780 cals.

The remarkable fact comes out that the *heat of neutralization* of these strong acids with a given base, sodium hydroxide, *is a constant.*

This suggests a further question very closely correlated to the above. Suppose we neutralize a given acid with a number of bases, will the heat liberated be a constant? and if so, will this bear any close relation to the above constant where the base was the same and the acid changed? This can be answered by the following results: —

	Heat of Neutralization
Hydrochloric acid and lithium hydroxide	13,700 cals.
Hydrochloric acid and potassium hydroxide	13,700 cals.
Hydrochloric acid and barium hydroxide	13,800 cals.
Hydrochloric acid and calcium hydroxide	13,900 cals.

The heat of neutralization of a given acid with a number of bases is also a constant. But what is even more surprising, the constant in this case has the same value as in the preceding

case where the base was unchanged, and the nature of the acid varied.

These facts when they were first discovered were very perplexing. Indeed, no satisfactory explanation of them could be furnished, and it was not until the theory of electrolytic dissociation was proposed that we could account for them at all.

Explanation of the Constant Heat of Neutralization of Strong Acids and Strong Bases. — It is one of the crowning glories of the theory of electrolytic dissociation, that it not only explains all of the facts in connection with the neutralization of strong acids and bases in dilute aqueous solution; but these facts are a necessary consequence of the theory.

Take, as an example, hydrochloric acid and sodium hydroxide. In a very dilute, aqueous solution of hydrochloric acid all the molecules are dissociated into hydrogen ions and chlorine ions thus: —

$$HCl = \overset{+}{H},\ \overset{-}{Cl}.$$

Similarly, in dilute, aqueous solution the molecules of sodium hydroxide are completely broken down into ions: —

$$NaOH = \overset{+}{Na},\ \overset{-}{OH}.$$

When the dilute aqueous solutions of the base and acid are brought together, the following reaction takes place: —

$$\overset{+}{Na},\ \overset{-}{OH} + \overset{+}{H},\ \overset{-}{Cl} = \overset{+}{Na},\ \overset{-}{Cl} + H_2O.$$

The cation of the base, sodium, and the anion of the acid, chlorine, remain in solution as ions after the process of neutralization in exactly the same condition as before neutralization took place. The anion of the base, hydroxyl, and the cation of the acid, hydrogen, combine and form a molecule of water. This is proved by the fact that water is always formed as the result of the process of neutralization.

Since hydroxyl is the anion of every base, and hydrogen the

cation of every acid, the process of neutralization of any strong acid with any strong base in dilute solution, consists in the union of the hydroxyl ion of the base with the hydrogen ion of the acid, forming a molecule of water.

The process of neutralization of any acid by any base is, therefore, exactly the same as the process of neutralization of any other acid by any other base. The total heat that is liberated when a gram-equivalent of a completely dissociated acid acts on a gram-equivalent of a completely dissociated base, is the heat set free by the union of a gram-equivalent of hydroxyl ions with a gram-equivalent of hydrogen ions. Thus: —

$$\overset{+}{\mathrm{H}}\,\mathrm{aq} + \overset{-}{\mathrm{OH}}\,\mathrm{aq} = 13{,}700 \text{ cals.}$$

Since all processes of neutralization of completely dissociated acids and bases are the same, the heat of neutralizatian of all such acids and bases must be a constant.

Indicators. — In order to determine when an acid and a base just neutralize one another, certain substances are used which have a different color in the presence of an acid from that in the presence of a base. Such substances are termed *indicators.* Take the organic coloring matter *litmus.* In the presence of an acid it is red. In the presence of a base it is blue. In neutral solution it is purple. By adding a few drops of a solution of litmus to any given solution we can tell whether the solution is acidic, basic, or neutral.

If we wish to just neutralize a base with an acid, we add the indicator to the solution of the base. The indicator is colored blue. Add the acid drop by drop until the solution becomes purple, which means that all the base has been neutralized and that the solution is neutral.

If we use the weak organic acid *phenolphthaleïn,* we will find that it is purplish red in the presence of bases, and colorless in the presence of acids.

Methyl orange, on the other hand, is deep red in the presence of acids, and yellow in the presence of alkalies.

EXPERIMENTS WITH ACIDS AND BASES

Experiment 66. Neutralization of Acids by Bases. — (Hydrochloric acid; sulphuric acid; nitric acid; sodium hydroxide; potassium hydroxide; barium hydroxide.)

Introduce 10 cc. of dilute hydrochloric acid into a beaker containing 50 cc. of water. Add a few drops of litmus. Just neutralize the solution with sodium hydroxide. If the water is now removed by evaporation, the cation of the base sodium will combine with the anion of the acid chlorine, and the salt, sodium chloride, will be formed. This will appear as a white mass when the solution is evaporated to dryness.

Proceed in an exactly similar manner with potassium hydroxide and sulphuric acid. On evaporating the water the cations of potassium will unite with the sulphuric anion, $\overline{\overline{SO}}_4$, forming potassium sulphate.

Perform the same experiment with nitric acid and barium hydroxide. On evaporation the barium nitrate will separate as a white powder.

In this connection see Experiment 44 in which salts of ammonium were formed. (See page 100.)

Experiment 67. Heat of Neutralization. — (Dilute hydrochloric acid; dilute sodium hydroxide.)

Introduce 50 cc. of dilute hydrochloric acid into one beaker, and an equal volume of dilute sodium hydroxide into another beaker. Introduce a thermometer into each beaker and note the temperatures. Pour slowly the acid into the alkali, with vigorous stirring. Read the thermometer immersed in the mixture. What do you note? Explain. (See page 101.)

Experiment 68. Indicators. — (Dilute acid; dilute alkali; litmus; phenolphthaleïn; methyl orange.)

Introduce 10 cc. of dilute sodium hydroxide into a beaker containing 100 cc. of water, and add a few drops of litmus until the solution shows a distinctly blue color. Add acid drop by drop, stirring vigorously with addition of each drop. As soon as the base is neutralized and even a slight excess of acid is added, the solution will turn deep red in color. Now add alkali, and the blue color will return again. As we have already seen, the blue color of litmus is characteristic of the presence of an alkali, and the red color shows that an acid is present.

Repeat the same experiment, adding to the alkali a few drops of an alcoholic solution of phenolphthaleïn. The beautiful red

color is a characteristic reaction of this indicator with alkalies. Add hydrochloric acid cautiously from a pipette, stirring after the addition of each drop. When the alkali has all been neutralized, the red color will disappear, and the solution will become colorless. Now add a little alkali, and the red color will return again.

Repeat the same experiment, using methyl orange. In the presence of an alkali it is slightly yellow in color. In the presence of an acid it is deep red.

These reactions show some of the methods which are at our disposal for detecting alkalies and acids. (See page 103.)

Experiment 69. Neutralization of Acids and Bases, Quantitative Work. — (Two burettes; dilute hydrochloric and sulphuric acids; dilute sodium and potassium hydroxides; methyl orange; litmus.)

Add 10 cc. of ordinary dilute hydrochloric acid to a 500 cc. measuring-flask, and fill the flask to the mouth with distilled water. Shake from time to time. Pour the solution into a bottle, and shake repeatedly until used.

In a similar manner prepare very dilute solutions of sulphuric acid, sodium hydroxide, and potassium hydroxide, using 5 cc. of "dilute" sulphuric acid and 20 cc. of each of the "dilute" bases, and diluting each to 500 cc. The apparatus to be used is shown in Figure 33. It consists of two burettes supported on a convenient stand. A burette is a long, narrow, glass tube, graduated to cubic centimetres. It is closed at the bottom by a rubber tube grasped by a pinch-cock. By pressing on the pinch-cock the tube is opened, and the liquid can flow out of the tube.

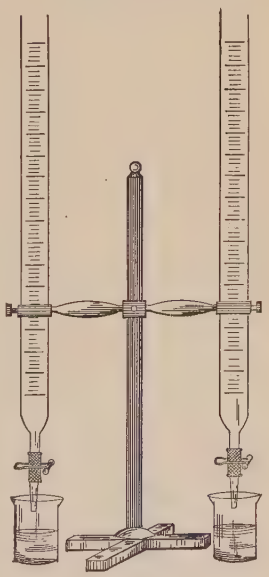

Fig. 33.

Fill one of the burettes with the dilute solution of hydrochloric acid, and the other with the dilute solution of sodium hydroxide. Run 25 cc. of the alkali into each of three small beakers and add two or three drops of methyl orange to each beaker. Run in the acid drop by drop, stirring vigorously

after the addition of each drop. Watch carefully for the appearance of the first trace of the red color of the indicator. This means that all of the alkali has been neutralized. Having read the burette before any acid was admitted, read it again. Note the amount of acid required to neutralize 25 cc. of the alkali. Repeat the experiment three times and see how closely the results agree in the three determinations.

Repeat the same experiment, using potassium hydroxide instead of sodium hydroxide.

Repeat the above experiments, using hydrochloric acid with both bases, and note the results.

Repeat one or two of the last experiments, using litmus as the indicator instead of methyl orange. Study thoroughly the numerical data obtained, and it will be found that a given amount of acid always requires a given amount of base to neutralize it. Show that this is the case.

CHAPTER XI

THE ATMOSPHERIC AIR AND CERTAIN RARE ELEMENTS OCCURRING IN IT

THE ATMOSPHERIC AIR

It was stated when we were studying nitrogen that the chief source of that element was the atmospheric air. Indeed, it comprises nearly four-fifths of the atmosphere. In addition to nitrogen, we find an abundance of oxygen in the atmosphere. This amounts to nearly one-fifth of the whole. In addition to these two elements we find many other substances, both elementary and compound, in the atmosphere, so that we must study this mixture of gases with some thoroughness.

Composition of the Atmosphere. — In order to determine the exact composition of the atmosphere, we must make a quantitative analysis of it. The oxygen in the air can be determined in several ways. A measured volume of air can be passed over heated copper. The oxygen combines with the copper, forming copper oxide. By weighing the tube containing the copper before the experiment, and weighing the tube containing the copper and copper oxide after the experiment, we know from the gain in weight the weight of the oxygen in a given volume of air. Knowing the weight of a litre of oxygen and of a litre of air, the percentage of oxygen can be calculated at once.

Again, the oxygen can be removed from the air by inserting a piece of phosphorus, which will combine with the oxygen. By measuring the original volume of the air, and the volume after all the oxygen has been removed, we have the percentage of oxygen by volume in the atmospheric air.

Results by the different methods show that the oxygen in the air is about 20.8 per cent by volume, and 23 per cent by weight.

The question arises, Does the amount of oxygen present remain constant, or does it vary from place to place or from time to time? While slight variations have been detected, pure air from different parts of the globe, and in different altitudes, varies very slightly in composition.

The remainder of the atmospheric air is nearly all *nitrogen*, a number of other substances, however, occurring in it in very small quantities. There are traces of *carbon dioxide* in the air. The amount can be determined by passing the air through a solution of barium hydroxide, and weighing the amount of barium carbonate precipitated.

The small quantity of *ammonia* in the air can be determined by passing a given volume of air through a solution of a standard acid, and determining how much of the acid is neutralized.

The air under all conditions contains *water-vapor*. The amount, however, varies greatly from time to time and from place to place.

To determine the amount of water-vapor in the atmosphere, it is only necessary to pass a measured volume of air over some good drying agent, such as phosphorus pentoxide, and determine the increase in the weight of the pentoxide.

Other substances may occur in the atmosphere in very minute quantities, such as *ozone*, *hydrogen dioxide*, *oxides of nitrogen*, and the like, but the quantities are so small that they can, for all practical purposes, be disregarded.

In addition to the constituents already named, there are a number of rare elements which occur in the air in very small quantities. These are the newly discovered elements, *argon*, *helium*, *neon*, *krypton*, and *xenon*. These elements we shall consider briefly a little later.

Is the Air a Mixture or a Compound? — The question naturally arises, Is the atmospheric air a chemical compound or a mechanical mixture? The fact that it has so nearly the same

composition the world over, would argue in favor of the oxygen and nitrogen being in combination, forming a definite compound. This line of argument, however, is by no means conclusive, since we might easily have the two gases mixed in essentially the same proportion in all regions. There is, however, direct evidence which shows that the air is simply a mechanical mixture of oxygen and nitrogen, and not a chemical compound.

When air is shaken with water, the part that dissolves has a very different composition from ordinary air. The latter contains in round numbers four parts of nitrogen to one of oxygen, while air which has been dissolved in water contains only 1.9 parts of nitrogen to one of oxygen. This is due to the fact that oxygen is much more readily soluble in water than nitrogen. If air is a compound of oxygen and nitrogen, the compound would dissolve as such, and the air which would be dissolved by water would have the same composition as ordinary air.

Again, chemical union is always accompanied, as we express it, by thermal change. Oxygen and nitrogen mix in the proportion to form air without any thermal change, and air is, therefore, not a chemical compound.

Physical Properties of Atmospheric Air. — The specific gravity of air varies slightly, just as the composition changes slightly. Under the average conditions of 0° and 760 mm. pressure, one litre of air weighs 1.293 grams. The pressure of the air, however, decreases very rapidly as we rise from the level of the sea, and a litre of air on the top of a high mountain would weigh much less.

Liquid Air. — We have seen that both oxygen and nitrogen can be liquefied, and would expect, therefore, that atmospheric air, which is essentially a mixture of these two gases, could also be liquefied. Such is the fact. The method employed is based on exactly the same principles that were made use of to liquefy oxygen and similar substances. The most economical method consists in compressing the air and removing the heat

set free by a stream of cold water. The compressed air is allowed to expand, when its temperature is very much lowered. It is then allowed to cool other compressed air, which, in turn, is allowed to expand, and a still lower temperature is produced. This is continued until a temperature is reached at which the compressed air, when allowed to expand, becomes partly liquefied. In this process the air is allowed to expand through a fine opening known as a *needle valve*, when part of the compressed air is liquefied and the remainder passes off as gas.

Liquid air has a slightly bluish color. When filtered from solid carbon dioxide and ice it is transparent. It boils at $-190°$. The liquid nitrogen, having a lower boiling-point than liquid oxygen, boils off more rapidly, and the liquid remaining after liquid air has been allowed to evaporate for a considerable time, is almost pure liquid oxygen.

ARGON, HELIUM, KRYPTON, NEON, XENON

Argon. — These five elements have all been discovered in atmospheric air since the summer of 1894. Just before this time Lord Rayleigh had observed that nitrogen obtained from atmospheric air by removing all known constituents was slightly heavier, volume for volume, than nitrogen prepared by heating ammonium nitrite.

The most probable explanation seemed to be that the nitrogen from the air contained some impurity which was heavier than nitrogen.

Rayleigh and Ramsay each isolated the gas, using, however, very different methods. Ramsay proceeded as follows: He determined to remove the oxygen from the air, then the nitrogen and other known constituents, and see if anything remained.

He removed the oxygen from the air by passing it over red-hot copper. The nitrogen was removed from the residue by passing it over red-hot magnesium, the ordinary impurities having been previously removed. There remained a residue

which spectrum analysis showed to be a new substance, and which was a little less than one per cent of the atmosphere. Ramsay and Rayleigh were not able to make it combine with any known substance, and from its chemical inactivity called it *argon*.

Helium, Neon, Krypton, and Xenon. — Since the discovery of argon, Ramsay has carried his investigations on the atmospheric air much farther, and has discovered four new substances, all of which appear to be elementary. When air is liquefied, two of these escape, being very volatile — helium and neon.

Helium, so called because it had been recognized by means of the spectroscope as occurring in the sun, has also been discovered in the waters of certain springs, and in certain ores of uranium. When a mixture of helium and neon is cooled in liquid hydrogen, the *neon* is liquefied, while the helium remains a gas. Helium does not combine with any known substance, and its boiling-point is somewhat lower than that of hydrogen. It has, then, the lowest boiling-point of any known substance, and has thus far not been liquefied.

Krypton and *Xenon* boil higher than air, and were, therefore, found in the residue from the evaporation of a large amount of liquid air. They were separated by means of the difference in their boiling-points.

EXPERIMENTS WITH ATMOSPHERIC AIR

Experiment 70. Determination of the Amount of Oxygen in the Atmosphere. — (Tall glass cylinder; glass tube closed at one end holding about 100 cc., and graduated into centimetres and millimetres; a piece of phosphorus attached to a bent wire.)

Arrange the apparatus as in Figure 1. Before introducing the phosphorus, bring the water inside the tube to the same level as outside and read the volume of the inclosed gas. Read the temperature of a thermometer attached to the glass tube; also the height of the barometer in the same room in which the experiment is being carried out. The reasons for making these readings will appear a little later.

Introduce the phosphorus and allow it to remain in the tube for at least 12 hours. Then remove the phosphorus. It will be seen at once that the volume of the gas has diminished. Bring the water to the same level inside and outside the tube by lowering the tube in the cylinder; read the volume of the residual gas, also the temperature and barometric pressure.

The reason for observing the temperature and pressure when making the above readings will appear from the following considerations.

The volume of a gas changes with the pressure to which the gas is subjected. The greater the pressure, the less the volume. Indeed, we know from *Boyle's law for gases* that the volume varies inversely as the pressure. From day to day the barometric pressure changes and therefore must be taken into account.

The volume of a gas also varies with the temperature — the higher the temperature the greater the volume, pressure being constant. For every rise in temperature of one degree centigrade the volume of a gas will increase $\frac{1}{273} = 0.003665$, which is the *law of Gay Lussac* for gases. Since temperature changes from time to time, this also must be taken into account.

In order that the volumes of gases as measured may be comparable, we must refer them to comparable conditions. The conditions which have been selected are a temperature of 0° C. and a pressure of 760 mm. of mercury.

Let the volume of the gas as read at $t°$ and p mm. of mercury pressure be v. The volume of this gas V at 0° and 760 mm. pressure will, from the above relations, be: —

$$V = \frac{vp}{760(1 + 0.003665\,t)}.$$

This takes into account every factor except the tension of the aqueous vapor in the tube. This pressure acts against the barometric pressure, so that the gas is really under less pressure than would be indicated by the barometer. This must be subtracted from the barometric pressure; we will represent the tension of the aqueous vapor by h. The true volume of the gas V at 0° and 760 mm. pressure would then be: —

$$V = \frac{v(p - h)}{760(1 + 0.003665t)}.$$

In both of the above readings calculate the true volume of the gas under standard conditions. It will be found that about *one-fifth* of the gas has combined with the phosphorus, or, more accurately, 21 per cent.

Air, therefore, contains approximately 21 per cent of oxygen. That the remaining gas is not oxygen can be shown by plunging into it a lighted match. It is mainly nitrogen, but contains quite a large number of other elements and compounds as we have seen; but these are present in very small quantities. (See page 107.)

Experiment 71. Detection of Carbon Dioxide in the Atmosphere. — (A large bottle; two glass cylinders; corks; glass tubing; rubber tubing; pinch-cock; barium hydroxide.)

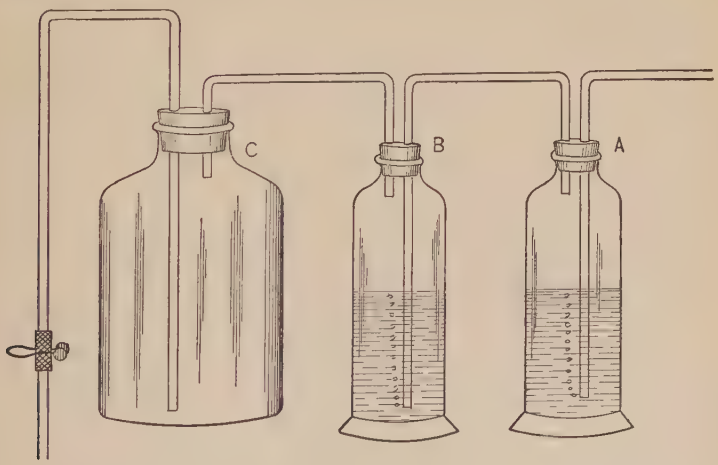

FIG 34.

Arrange an apparatus as shown in Figure 34. The large glass bottle *C* is filled with water. The glass cylinders contain a solution of barium hydroxide. Allow the water to flow slowly out of the end of the tube, by opening the pinch-cock, which closes the rubber tube. As the water flows out, air will pass in through the cylinders *A* and *B*, into *C*. A white precipitate will be formed in *A* and *B*, but will be much heavier in *A* than in *B*. Barium hydroxide combines readily with carbon dioxide, forming barium carbonate, which is a white solid, insoluble in water. Most of the carbon dioxide in the air combines with

the barium hydroxide in the first cylinder; a little, however, passes on to the second cylinder and there combines with barium hydroxide. This explains why a heavier precipitate is formed in *A* than in *B*.

After the vessel *C* has become half full of air, remove the cork and add quickly some barium hydroxide — closing the apparatus again as quickly as possible. The barium hydroxide in *C* will become only slightly cloudy, showing that practically all of the carbon dioxide has been removed from the air in passing through the solutions in *A* and *B*. (See page 108.)

Experiment 72. Proof of the Presence of Water in the Air. — (Two large ground-glass stoppered weighing-tubes; calcium chloride; phosphorus pentoxide.)

Fill a ground-glass stoppered weighing-tube about one-half full with calcium chloride. Insert the stopper and weigh the tube. Remove the stopper and expose to the air for several hours. What evidence have you that water has been absorbed? Insert the stopper and reweigh the tube. Has it gained in weight?

Perform exactly the same experiment with phosphorus pentoxide. Does it increase in weight? (See page 108.)

CHAPTER XII

DETERMINATION OF RELATIVE ATOMIC WEIGHTS

Combining Numbers and Atomic Weights. — We saw in Chapter VI that the atomic theory was proposed to account for certain well-established laws of chemical combination — the laws of definite and multiple proportions. If atoms are the ultimate units of matter, these must have definite weights, and it is obviously of great importance for chemistry to determine the relative weights of the atoms of different substances.

If the same number of atoms of any two substances combine, the relative weights of the substances that combine represent the relative weights of the atoms which enter into combination. This apparently furnishes a means of determining relative atomic weights. It is only necessary to determine the relative weights of substances that combine — the combining numbers — in order to ascertain the relative weights of the atoms of these substances. This would be true if a given number of atoms of one substance always combined with an equal number of atoms of another. But we know that this is not the case, since it often happens that two elementary substances combine in several proportions. To determine the relative atomic weights of the elements, we must, therefore, know the combining numbers of the elements, and also the number of atoms of the different elements which combine with one another. We will take up first the method of determining the combining numbers of the elements.

Chemical Methods of determining Combining Numbers. — The simplest method would be to take some element as our standard, and call its combining number one. Then allow all of

the other elements to combine with this one, and determine the weights of the different elements which combined with unit weight of our standard element. Since hydrogen has the smallest combining number, it would naturally be chosen as the unit. The problem then would be to determine, say, the number of grams of the different elements which combine with one gram of hydrogen, and these figures would represent the combining weights of the elements in terms of hydrogen as unity. We might thus work out a table of the combining numbers of all of the elements in terms of hydrogen as unity.

This part of the problem is, however, not as simple as would be indicated from the above. Some of the elements combine with hydrogen in more than one proportion. We would thus obtain different combining numbers for the same element, depending upon which of its compounds we selected.

It is perfectly clear that neither the chemical analysis of the compound, nor its synthesis from the elements, throws any light on the problem as to the number of atoms of one substance combined with one atom of the other. Other methods must be employed in order to determine the number of atoms of the one element which have combined with one atom of the other. To these we shall now turn.

Avogadro's Hypothesis. — Avogadro, in 1811, taking into account all of the facts known, advanced the hypothesis that —

In equal volumes of all gases, at the same temperature and pressure, there is an equal number of ultimate parts or molecules.

Avogadro extended his hypothesis to all gases, including even the elementary gases, and regarded the molecules of these substances as made up of atoms of the same kind, which had united with one another. This was a necessary consequence of his hypothesis. One volume of hydrogen gas combines with one volume of chlorine gas, and forms two volumes of hydrochloric acid gas. If there are the same number of molecules in equal volumes of all gases, there would be twice as many in the two volumes of hydrochloric acid as in the one

volume of hydrogen, or the one volume of chlorine. Since each molecule of hydrochloric acid must contain at least one atom of hydrogen and one atom of chlorine, the molecule of hydrogen and of chlorine must be made up of at least two atoms. The hypothesis of Avogadro has been confirmed by such an abundance of subsequent work, in so many directions, that it is now placed among the well-established laws of nature.

Avogadro's Hypothesis and Molecular Weights. — Given the hypothesis of Avogadro, the determination of the relative molecular weights of gases is very simple. If there is an equal number of molecules contained in equal volumes of the different gases, the relative weights of equal volumes of these gases give at once the relative weights of the molecules contained in them. It is only necessary to choose some substance as our standard, and express the molecular weights of other substances in terms of this standard. We would naturally select as the unit that substance which has the smallest density, and this is hydrogen. From what has been said, however, in reference to the union of hydrogen and chlorine, forming hydrochloric acid, it is certain that the molecule of hydrogen contains at least two atoms. We will, therefore, call the molecular weight of hydrogen two, and calculate the molecular weights of other elements in terms of this standard. The densities of substances are usually determined in terms of air as the unit. It is a simple matter to recalculate these in terms of hydrogen as two. The density of hydrogen in terms of air as the unit is 0.0696. We must multiply this by 28.73 to obtain our new unit 2 ($2 \div 0.0696 = 28.73$). Similarly, for other substances whose densities are known with reference to air; these densities must be multiplied by the constant 28.73 to transform them into densities in terms of hydrogen = 2. These latter values are the relative molecular weights of the substances in the form of gas, referred to the molecular weight of hydrogen as two.

Method of Dumas for determining Vapor-densities. — The method of Dumas consists in determining the amount of sub-

stance which, in the form of vapor, at a given temperature, just fills a flask whose volume is afterwards ascertained. The flask is weighed full of air. Knowing the volume of the flask, we know the weight of air contained in it; therefore, we know the weight of the empty flask. The weight of the flask being known, and the weight of the flask plus the substance which just filled it with vapor, we know the weight of the substance. By determining the weights of the vapors of different substances which fill a flask of given volume, we have the relative densities of the vapors.

Fig. 35.

The apparatus used is a balloon flask (Fig. 35) holding from 200 to 300 cc.

The flask is carefully dried and weighed.

A few grams of the substance whose vapor-density is to be determined are introduced into the flask, the neck drawn out to a capillary, and the flask placed in a bath which is at least ten or fifteen degrees above the boiling-point of the substance. The substance vaporizes, and drives out the air, and when the vapor of the substance ceases to escape, the capillary is fused shut. The flask after cooling is weighed. The fine point is then cut off under mercury and the flask filled with mercury. The flask may then be weighed again, or the mercury poured out and measured, giving the volume of the flask.

Results of Vapor-density Measurements. — A few results are given in the following table, showing in column I the densities in terms of air as the unit; in column II the densities or relative molecular weights in terms of hydrogen = 2. The results in column II are obtained by multiplying the results in column I by 28.73.

	I		II
Hydrogen, 0° C. . .	0.06926		2
Oxygen, 0° C. . . .	1.10563		31.76
Nitrogen, 0° C. . . .	0.9713		27.90
Sulphur, 1400° C. . .	2.17	× 28.73	62.34
Chlorine, 200° C. . .	2.45		70.38
Bromine, 100° C. . .	5.54		159.16
Mercury, 1400° C. . .	6.81		195.65
Iodine, 940° C. . . .	8.72		250.52

Atomic Weights from Molecular Weights. — If we knew the number of the atoms contained in the molecules of elements in the gaseous state, the problem of relative atomic weights would be solved at once by dividing the molecular weight of the gas by the number of atoms in the molecule. The problem is, however, not as simple as this, since we do not know at once the number of atoms in the molecules of elements. Other lines of thought have enabled us to solve this, the second part of our problem.

The definition of an atom as an indivisible particle of matter shows that fractions of atoms cannot exist. No molecule can contain a fraction of any atom. The quantity of any substance which enters into a molecule must be at least one atom. It may be more than one, but it cannot be less. This is the key to the problem. Suppose we wish to determine the number of hydrogen atoms in a molecule of hydrogen. We must examine compounds into which hydrogen enters, and find out what is the smallest quantity of hydrogen which enters into the molecule of the compound. Let us take hydrochloric acid, whose molecular weight is 36.45. This is shown by analysis to be composed of 1 part of hydrogen and 35.45 parts of chlorine. This 1 part of hydrogen is at least one atom; it may be more, but it cannot be less. By examining a large number of compounds into which hydrogen enters, it has been found that hydrogen never enters into a molecule of any substance in a

smaller quantity than in hydrochloric acid. This is, therefore, for us the atom of hydrogen, but it may in reality be composed of a great number of smaller parts. The hydrogen that enters into the molecule of hydrochloric acid is just half the quantity that forms the molecule of hydrogen gas, since one volume of hydrogen combining with one volume of chlorine yields two volumes of hydrochloric acid gas. The molecule of hydrogen, therefore, contains at least two atoms, and since there is no experimental reason for assuming that it contains more than two, we say that the molecule of hydrogen is made up by the union of two hydrogen atoms. Knowing the number of atoms in the molecule, the atomic weight follows at once from the molecular weight determined by vapor-density, and corrected by the most refined methods of chemical analysis.

By methods similar to the above the molecules of many elements have been shown to be composed of two atoms. But this by no means applies to all elementary substances. The molecules of some elementary substances contain more than two atoms, and in a very few cases the molecule and atom seem to be identical.

The relations between the molecular weights of a few of the elements and their atomic weights are given in the following table: —

Elements	Atomic Weights	Molecular Weights
Hydrogen	1	2
Nitrogen	14.01	28.02
Oxygen	15.88	31.76
Phosphorus	30.96	123.84
Sulphur	31.98	{ 63.96 above 800° C. { 191.88 at 500° C.
Chlorine	35.18	70.36
Arsenic	74.9	299.6
Cadmium	111.7	111.7
Mercury	199.8	199.8

This table brings out a number of facts of interest. The molecular weight of a number of the elements is twice as great as the atomic weight. In some cases, as with sulphur, the molecular weight is twice the atomic weight at a given temperature, and then varies with the temperature. In the cases of cadmium and mercury the molecular weights are apparently identical with the atomic weights. The molecular weights of phosphorus and arsenic are four times the atomic weights.

The Relative Weights of the Atoms. — In determining atomic weights we must choose some element as our standard. We would naturally take the lightest element, hydrogen, and call it unity. This has been done, and all atomic weights referred to this unit. But it is unfortunately true that hydrogen does not combine directly with many of the elements and form stable compounds that can be analyzed.

Oxygen, on the other hand, does combine with a large number of the elements, forming some of the most stable compounds with which we are acquainted. It, therefore, seemed best to compare the atomic weights of the elements directly with the atomic weight of oxygen, which we will call 16, since it is approximately 16 times the atomic weight of hydrogen, and then compare oxygen with hydrogen, with which it forms the very stable compound, water.

Table of Atomic Weights. — The most probable atomic weights of the elements, based upon the best determinations, are given in the following table: —

Element	Atomic Weight	Element	Atomic Weight
Aluminium	27.1	Cadmium	112.35
Antimony	120.0	Cæsium	132.9
Argon	39.9	Calcium	40.1
Arsenic	75.0	Carbon	12.0
Barium	137.4	Cerium	140.0
Bismuth	208.3	Chlorine	35.45
Boron	11.0	Chromium	52.1
Bromine	79.96	Cobalt	59.0

Element	Atomic Weight	Element	Atomic Weight
Columbium	94.0	Potassium	39.14
Copper	63.6	Praseodymium	140.45
Erbium	166.0	Radium	257.8
Fluorine	19.05	Rhodium	103.0
Gallium	70.0	Rubidium	85.4
Germanium	72.5	Ruthenium	101.7
Glucinum	9.1	Samarium	150.0
Gold	197.25	Scandium	44.1
Helium	4.0	Selenium	79.2
Hydrogen	1.01	Silicon	28.4
Indium	114.0	Silver	107.93
Iodine	126.85	Sodium	23.05
Iridium	193.0	Strontium	87.68
Iron	55.9	Sulphur	32.06
Krypton	81.75	Tantalum	183.0
Lanthanum	138.8	Tellurium	127.6
Lead	206.9	Terbium	160.0
Lithium	7.03	Thallium	204.1
Magnesium	24.36	Thorium	232.5
Manganese	55.0	Thulium	171.0?
Mercury	200.0	Tin	119.0
Molybdenum	96.0	Titanium	48.15
Neodymium	143.6	Tungsten	184.0
Neon	20.0	Uranium	238.5
Nickel	58.7	Vanadium	51.4
Nitrogen	14.04	Xenon	128.0
Osmium	191.0	Ytterbium	173.0
Oxygen	16.0	Yttrium	89.0
Palladium	106.5	Zinc	65.4
Phosphorus	31.0	Zirconium	90.6
Platinum	195.0		

The Quantitative Method of Dealing with Chemical Reactions. — Thus far we have dealt qualitatively with chemical reactions — have studied what substances react and what products are formed. We have not raised the question as to how much of each substance entered into the reaction and how much of each product was formed.

Knowing the relative weights of the atoms, we can now deal quantitatively with reactions, and from given quantities of substances calculate the amounts of the products formed. We shall now apply this method to some of the reactions already studied.

PROBLEMS IN CONNECTION WITH OXYGEN

1. Calculate the weight of oxygen obtainable from 4 grams of potassium chlorate.[1]

2. What would be the volume of oxygen obtainable from 5 grams of manganese dioxide? (One litre of oxygen weighing 1.4296 grams.)

3. How many grams of mercury oxide would be required to yield 20 litres of oxygen? How many to yield 20 grams of oxygen?

4. What would be the weight and volume of oxygen required to combine with 10 grams of sulphur to form sulphur dioxide?

5. What would be the weight of phosphorus required to combine with 15 litres of oxygen to form phosphorus pentoxide? What would be the weight of the product formed?

6. With what volume of oxygen would 5 grams of carbon combine to form carbon dioxide?

PROBLEMS IN CONNECTION WITH HYDROGEN

1. Weight and volume of hydrogen that can be obtained by decomposing 5 grams of water with sodium? (One litre of hydrogen weighing 0.08995 gram.) By dissolving 1 gram of zinc in hydrochloric acid?

[1] The solution of such problems is comparatively simple. Potassium chlorate has the formula $KClO_3$. The molecular weight of this compound is obtained by adding the atomic weights of the atoms in the compound.

At. wt. K =	39.14
At. wt. Cl =	35.45
At. wt. O = 16×3 =	48.00
	122.59

The molecular weight of potassium chlorate is to the atomic weight of oxygen multiplied by the number of atoms of oxygen set free from each molecule of the salt as the weight of potassium chlorate is to x: —

$$122.59 : 48 = 4 : x.$$

2. What volume of hydrogen will combine with 5 grams of oxygen to form water?
3. Weight of copper oxide which would be reduced to metallic copper by 3 litres of hydrogen gas?
4. What volume of hydrogen would combine with oxygen to form 3 grams of water?
5. How much hydrogen (weight and volume) would be obtained by electrolyzing 2 grams of water?
6. Volume of water-vapor formed when 3 grams of oxygen combine with hydrogen?

PROBLEMS IN CONNECTION WITH CHLORINE

1. Weight and volume of chlorine obtainable from 1 gram of hydrochloric acid? (One litre of chlorine weighing 3.22 grams.)
2. Weight of copper which would combine with 1 litre of chlorine?
3. Volume of chlorine which would combine with 1 litre of hydrogen? with 1 gram of hydrogen? What would be the volume of the hydrochloric acid formed in each case?
4. How much sodium chloride would be required to yield the chlorine which would combine with 2 grams of hydrogen?
5. Weight of potassium chlorate which could be formed from all the chlorine in 3 grams of bleaching-powder?

PROBLEMS IN CONNECTION WITH NITROGEN

1. When 3 grams of ammonium nitrite are decomposed by heat, what is the weight of the nitrogen obtained? What is the volume? (One litre of nitrogen weighing 1.2575 grams.)
2. With what volume of ammonia would 2 grams of hydrochloric acid combine? (One litre of ammonia weighing 0.775 grams.)
3. What amount of ammonium nitrite must be decomposed by heat to yield one gram of nitrous oxide?
4. When 5 grams of sodium nitrite are decomposed by sulphuric acid, what weight of nitrogen sesquioxide is set free?
5. What would be the weight of the nitric acid formed by treating 7 grams of sodium nitrate with the quantity of sulphuric acid required to produce the acid sulphate, $NaHSO_4$?

PROBLEMS IN CONNECTION WITH THE VOLUME OF GASES

1. If the volume of a dry gas at 0° and 729 mm. pressure is 50 cc., what would be its volume under normal conditions (*i.e.* 0° and 760 mm. pressure)? [1]

2. If the volume of a dry gas at 10° and 760 mm. pressure is 25 cc., what would be its volume under normal conditions?

3. If the volume of a gas over water at 20° and 745 mm. pressure is 35 cc., what volume would it have at normal temperature and pressure (the pressure of the aqueous vapor at 20° being 17.4 mm.)?

[1] The solution is as follows: —

The equation for the volume of a gas under normal conditions, as developed on page 112, is $V = \frac{v(p - h)}{760(1 + 0.003665\, t)}$.

$v = 50$,
$p = 729$,
$h = 0$, since the gas is dry;
$t = 0$.

Substituting these values in the above equation, we have: —

$$V = \frac{50(729)}{760(1 + 0)}.$$

CHAPTER XIII

THE PERIODIC SYSTEM

Relations between Atomic Weights and Properties of the Elements. — Almost as soon as the atomic weights of the elements were determined, chemists began to look for relations between the atomic weights of the elements and their properties. A number of such relations were pointed out, however of not very wide-reaching significance.

The Periodic System. — The first to point out the most important features in the arrangement of the elements according to their atomic weights was the Russian, Mendeléeff. In 1869 he arranged the elements in a table in the order of their atomic weights, and showed clearly that there is a periodic recurrence of properties as the atomic weights increase. This will be seen best in the following table, which is essentially the same in principle as that of Mendeléeff. Some elements unknown at the time the original system was proposed are introduced, and the present atomic weights of the elements are given.

The elements in group 0 are rare elements occurring in the air, and, as we have seen, have been recently discovered. The elements scandium, gallium, and germanium were unknown when Mendeléeff proposed his table. He, however, predicted their existence, their properties, and the properties of their compounds. These predictions have been fulfilled in a most beautiful manner, and this is one of the crowning glories of the periodic system.

All the elements are arranged in succession in the order of their increasing atomic weights. If we start with the element

Series	Group 0	Group I RH R_2O	Group II RH_2 RO	Group III RH_3 R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII RO
1		H = 1.01							
2	He = 4.0	Li = 7.03	Gl = 9.1	B = 11.0	C = 12.0	N = 14.04	O = 16.0	F = 19.05	
3	Ne = 20.0	Na = 23.05	Mg = 24.36	Al = 27.1	Si = 28.4	P = 31.0	S = 32.06	Cl = 35.45	
4	A = 39.9	K = 39.14	Ca = 40.1	Sc = 44.1	Ti = 48.15	V = 51.4	Cr = 52.1	Mn = 55.0	Fe = 55.9, Ni = 58.7 Co = 59.0, Cu = 63.6
5	–	(Cu = 63.6)	Zn = 65.4	Ga = 70.0	Ge = 72.5	As = 75.0	Se = 79.2	Br = 79.96	
6	Kr = 81.75	Rb = 85.4	Sr = 87.68	Y = 89.0	Zr = 90.6	Cb = 94.0	Mo = 96.0		Ru = 101.7, Rh = 103.0 Pd = 106.5, Ag = 107.93
7	—	(Ag = 107.93)	Cd = 112.35	In = 114.0	Sn = 119.0	Sb = 120.0	Te = 127.6	I = 126.85	
8	Xe = 128.0	Cs = 132.9	Ba = 137.4	La = 138.8	Ce – Yb[1] 140 – 173	Ta = 183.0	W = 184.0	—	Os = 191.0, Ir = 193.0 Pt = 195.0, Au = 197.25
9	—	(Au = 197.25)	Hg = 200.0	Tl = 204.1	Pb = 206.9	Bi = 208.3	—	—	
10	—		—	—	Th = 232.5	U = 238.5	—	—	

[1] This includes a number of the rare elements whose atomic weights range from 140 to 173.

with the smallest atomic weight next to hydrogen, *i.e.* lithium, and arrange the succeeding elements in the order of their atomic weights up to fluorine, we find that the next element, sodium, has properties quite similar to those of lithium. If we place sodium in the same vertical column with lithium, and then arrange the next elements in the order of their atomic weights, we find that magnesium falls in the same column with glucinum or beryllium, aluminium with boron, silicon with carbon, phosphorus with nitrogen, sulphur with oxygen, and chlorine with fluorine. This is, of course, a remarkable relation, since in every case those elements that fall in the same vertical column resemble each other very closely. The first seven elements, starting (not with hydrogen, since it does not fit into this scheme) with lithium, and ending with fluorine, agree very closely in properties with the second set of seven elements arranged as in the above table. We come now to the first member of the next series of seven elements, — potassium; it falls right into the group with lithium and sodium, calcium with glucinum and magnesium, titanium with carbon and silicon, vanadium with nitrogen and phosphorus, chromium with oxygen and sulphur, and manganese with fluorine and chlorine. Here again striking analogies appear between the different members in the same groups. The blank space between calcium and titanium contained no known element when this table was prepared. The element has since been discovered. After we leave manganese we encounter one of the weakest points of the Periodic System. The next elements in order of atomic weights are iron, cobalt, and nickel; but it is obvious that neither of these can be placed in the same group with the alkali metals. They must, therefore, be set aside and left out of the system. Then we come to copper, which is very questionably placed with the members of group I. Then irregularities appear again. At the end of the sixth series we find three or four more elements which do not fit into the scheme, but after leaving these, regularities again begin to manifest themselves.

The above suffices to show the general relation, and also the periodic recurrence of properties with increase in the atomic weights.

CHEMICAL PROPERTIES AND ATOMIC WEIGHTS. COMBINING POWER

If we start with lithium and proceed to the right along the second series, this striking fact is observed: the elements increase in their power to combine with oxygen regularly from left to right. Take first the power of the elements to combine with oxygen. Lithium forms the compound Li_2O, beryllium BeO, aluminium Al_2O_3, carbon CO_2, nitrogen N_2O_5; oxygen and fluorine may be disregarded for the moment. Take the third series. Sodium forms the compound NaO which is a superoxide, magnesium MgO, aluminium Al_2O_3, silicon SiO_2, phosphorus P_2O_5, sulphur SO_3, and chlorine Cl_2O_7. The fourth and fifth series show the same regularities, and similar relations are observed throughout the table. The best example of an element octivalent towards oxygen is osmium, which forms the compound OsO_4. We have, then, NaO, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, Cl_2O_7, OsO_4.

We may say in general that the power of the elements to combine with oxygen is smallest in group I, and increases regularly by unity in each succeeding group; reaching a maximum in group VIII, where, at least in the case of osmium, it is eight.

Results of a similar character are obtained if we study the power of the elements to combine with chlorine. Sodium combines with one chlorine atom, magnesium with two, aluminium with three, silicon with four, phosphorus with five. Sulphur does not combine directly with six chlorine atoms, but combines with both oxygen and chlorine, forming the compound SO_2Cl_2, in which the sulphur has a valence of four towards the oxygen, and of two towards the chlorine, or of six in all. But there is a member of group VI which combines directly with six chlorine

atoms. This is tungsten, in the tenth series. We would express the combining power of the elements towards chlorine as follows: —

$$NaCl,\ MgCl_2,\ AlCl_3,\ SiCl_4,\ PCl_5,\ SO_2Cl_2,\ (WCl_6)$$

Exactly the same regularity which was observed in the case of oxygen exists here. The elements in group I have the smallest power to combine with chlorine, and this increases by unity from group to group as we pass from left to right; reaching a maximum of six in the sixth group. We know of no element which has the power of combining directly with more than six atoms of chlorine.

When we examine the power of the elements to combine with hydrogen, a regularity is observed, but of a different kind from those already considered. Some of the elements in groups I, II, and III combine with hydrogen, forming *hydrides*, and these have the compositions in general indicated in the table. When we come to group IV, we find in carbon a remarkable power to combine with hydrogen. The highest valence of the elements towards hydrogen is manifested in this group, where one atom of the element combines directly with four atoms of hydrogen. As we pass to the right, the power of the elements to combine with hydrogen decreases, and decreases regularly. Nitrogen combines with three atoms of hydrogen, oxygen with two, and fluorine with one: —

$$NaH,\ CaH_2,\ BH_3,\ CH_4,\ NH_3,\ OH_2,\ FH.$$

The valence towards hydrogen increases from group I to group IV, where it reaches a maximum, and diminishes regularly as the valence towards oxygen increases.

The relations pointed out between the combining power of the elements are general, extending throughout the table of the elements. It should, however, be stated here that there are many breaks in the system, irregularities appearing in many places.

Basic and Acid Properties

At least one other relation between the chemical properties of the elements and their atomic weights must be pointed out. In any given series the element with the lowest atomic weight has the smallest power to combine with oxygen, as has already been stated. It has also the strongest basic character. Thus, lithium is more basic than glucinum, which, in turn, is far more basic than boron. Sodium is more basic than magnesium, while aluminium begins to show acid properties in its hydroxide. Potassium is far more basic than calcium, rubidium than strontium, cæsium than barium. The difference between copper and zinc, and silver and cadmium, is not so striking. As we find the most basic elements in the first group, we would expect to find the most acid in the last, and such is the case. Through the middle groups we find elements which show, now more, now less, basic or acid properties, depending upon conditions; but in the last column of the last well-defined group we have elements which manifest only acid-forming properties. The hydrogen and hydroxyl compounds of the halogens are always acids, and always react as such with all other substances. These facts are very surprising. As we pass upward in the table of atomic weights, say from oxygen, the first element we encounter is fluorine, with very pronounced acid-forming properties. The element with the next higher atomic weight is sodium, which is one of the strongest base-forming elements. Similarly, next to sulphur comes chlorine, which has stronger acid-forming properties than sulphur, but next to chlorine comes potassium, which is one of the most strongly basic elements. In the same way bromine is followed by rubidium, and iodine by cæsium, where the contrast in properties is quite as great as in the cases referred to above.

Many other relations between chemical properties and atomic weights have been pointed out, but those already considered are among the most important.

General Scheme to be Followed. — In dealing with the remaining elements we shall be guided largely by the Periodic System. This system, however, is defective, and we shall, therefore, not follow it blindly, but depart from it whenever the relations can be more clearly established by doing so.

We shall begin with the members of group VII in Mendeléeff's table, omitting, however, one member, manganese, which will not be taken up until much later.

We shall then take up some of the members of group VI — sulphur, selenium, and tellurium; while chromium, molybdenum, tungsten, and uranium will not be referred to until very much later. The nitrogen group (V) will then be studied, and following this the carbon group (IV).

The metallic elements will then be taken up. Groups I and II will be studied very nearly in the order indicated in the Periodic System, while the remaining metallic elements will be studied more or less independent of the system.

CHAPTER XIV

BROMINE, IODINE, FLUORINE

BROMINE (At. Wt. = 79.96)

Occurrence and Preparation. — The element bromine closely resembles the element chlorine. Like the latter it does not occur in the free condition in nature, and exists in very much smaller quantity than chlorine. The compounds of bromine, like those of chlorine, being in general very soluble, the chief occurrence of bromine is in the waters of the sea. Where sea-water has evaporated and deposited the great salt beds of the earth, we find the bromides mixed with a large number of other salts.

Bromine is prepared by three methods: The electrolysis of bromides, which is strictly analogous to the electrolysis of chlorides, the bromine ion passing to the anode and separating in the free condition, while the metal passes to the cathode.

A second method which was much used formerly, but is now seldom employed on the large scale, consists in the oxidation of hydrobromic acid by manganese dioxide; the hydrobromic acid being set free from the bromide by means of sulphuric acid: —

$$2\,NaBr + H_2SO_4 = Na_2SO_4 + 2\,HBr;$$
$$2\,HBr + MnO_2 + H_2SO_4 = MnSO_4 + 2\,H_2O + Br_2.$$

Combining these in one equation, we have —

$$2\,NaBr + MnO_2 + 2\,H_2SO_4 = MnSO_4 + Na_2SO_4 + 2\,H_2O + Br_2.$$

The third method consists in the replacement of bromine from bromides by means of chlorine: —

$$2\,KBr + Cl_2 = 2\,KCl + 2\,Br.$$

This method finds extensive use to-day.

Chemical Properties of Bromine. — Bromine in its chemical properties strikingly resembles chlorine. Like the latter it unites directly with most of the elements. The compounds formed — the bromides — are not as stable as the chlorides. This is shown by the fact that chlorine replaces bromine from the bromides. The bromides, like the chlorides, are in general soluble in water, the bromides being more soluble than the chlorides.

Bromine has a remarkable power to disintegrate organic substances. Its action upon the mucous membrane of the throat and nose is more vigorous than that even of chlorine, and great precaution must, therefore, be taken in working with the substance, to be protected from its disintegrating fumes.

Detection of Bromine. — The chemical properties of bromine are so closely allied to those of chlorine that it might at first sight seem difficult to determine with which we are dealing. This difficulty is, however, only apparent. If a bromide is treated with chlorine, the bromine, as we have seen, is set free and can be recognized by its odor and color. If a solution of a bromide is treated with a little chlorine water, a little carbon bisulphide being added to the tube and shaken vigorously, the bromine which has been set free by the chlorine is dissolved by the carbon bisulphide, and imparts its characteristic reddish brown color to the solution.

Bromine Atoms and Bromine Ions. — Bromine in the atomic condition behaves very differently from bromine in the ionic condition. The bromine ions when brought in contact with the silver ions combine with them at once, forming the characteristic precipitate, silver bromide.

$$\overset{+}{K}, \overset{-}{Br} + \overset{+}{Ag}, \overset{-}{NO_3} = \overset{+}{K}, \overset{-}{NO_3} + AgBr.$$

When bromine in the un-ionized condition is brought into the presence of silver ions, it does not combine to the slightest extent with the silver ions.

Physical Properties of Bromine. — The reddish brown liquid, bromine, has a density 3.1. It boils at 63°, yielding a reddish yellow vapor. The density of the vapor is 160, in terms of hydrogen as two. The atomic weight being 80, the molecule of bromine contains two atoms, or has the composition represented by the formula Br_2. Bromine solidifies at − 7°, forming an orange-red solid.

Bromine dissolves in water, forming what is known as *bromine water*, which is analogous to chlorine water. The saturated solution in water contains about 3 per cent of bromine.

Hydrobromic Acid. — A method of preparing hydrobromic acid is by allowing water to act upon the bromides of certain acid-forming elements such as phosphorus. The reaction that takes place in this case is: —

$$PBr_5 + H_2O = POBr_3 + 2\ HBr,$$

resulting in the formation of phosphorus oxybromide and hydrobromic acid.

The question which would naturally be asked is, Why not prepare hydrobromic acid by the action of sulphuric acid on bromides? This would be analogous to the preparation of hydrochloric acid by the action of sulphuric acid on chlorides.

This method is possible, but precautions must be taken, or a secondary reaction between the hydrobromic acid formed and the sulphuric acid takes place, which interferes with the value of the method. The sulphuric acid may be reduced to sulphur dioxide: —

$$2\ KBr + H_2SO_4 = K_2SO_4 + 2\ HBr;$$
$$H_2SO_4 + 2\ HBr = 2\ H_2O + 2\ Br + SO_2.$$

Properties of Hydrobromic Acid. — Hydrobromic acid resembles hydrochloric acid very closely in its chemical and physical properties.

Hydrobromic acid is a reducing agent. It is also a very strong acid, but not quite as strong as hydrochloric acid. A

dilute, aqueous solution of hydrobromic acid is completely dissociated into its ions: —

$$HBr = \overset{+}{H},\ \overset{-}{Br}.$$

The bromine ions manifest their presence by combining with the silver ions when brought in contact with them, forming the white precipitate, silver bromide, which is soluble with difficulty in ammonia.

When chlorine is brought into the presence of a bromide, the bromine separates, and chlorine passes into solution. If we examine this reaction more closely, we find that what has taken place is a transfer of the electrical charge from the bromine ion to the chlorine atom, converting the latter into an ion, while the bromine ion having lost its charge is converted into an atom. The reaction that takes place would be represented thus: —

$$\overset{+}{H},\ \overset{-}{Br} + Cl = \overset{+}{H},\ \overset{-}{Cl} + Br.$$

Compounds of Bromine with Oxygen and Hydrogen. — Bromine forms two well-characterized acids with oxygen and hydrogen. These are *hypobromous* and *bromic acids*. While hydrobromic acid is less stable than hydrochloric, as we have seen, oxygen acids of bromine are more stable than the corresponding acids of chlorine.

The sodium salt of hypobromous acid is prepared by the action of bromine on sodium hydroxide: —

$$2\,NaOH + 2\,Br = H_2O + NaBr + NaOBr.$$

This method of preparing sodium hypobromite is strictly analogous to the method of preparing sodium hypochlorite.

The best method of preparing bromic acid, is by the action of bromine on caustic potash. A mixture of potassium bromide and bromate is formed: —

$$6\,KOH + 3\,Br_2 = 5\,KBr + KBrO_3 + 3\,H_2O.$$

From this mixture the potassium bromate can be readily separated by *fractional crystallization*, — the same method

which was employed to separate potassium chlorate from potassium chloride. The bromate is much less soluble in water than the bromide, and readily crystallizes from a not too dilute solution of the two salts in water.

Bromic acid is obtained from potassium bromate by methods strictly analogous to those employed for obtaining chloric acid from potassium chlorate.

IODINE (At. Wt. = 126.85)

Occurrence and Preparation. — Iodine, named from the violet-blue color of its vapor, occurs very rarely in the free condition. It is widely distributed in nature, existing, however, usually only in small quantities. It occurs along with chlorides and bromides, but in very much smaller quantities than either of these substances. It is also contained in sea-water, as we would expect, on account of the solubility of its compounds. It is taken up from the waters of the sea by certain sponges and plants, and exists in considerable quantity in the ashes of such plants.

Iodine is obtained to-day mainly from Chili saltpetre, in which it occurs in the form of sodium iodate. The iodine is obtained from this salt by reduction with sulphurous acid.

When an iodide is treated with manganese dioxide and sulphuric acid, the following reaction takes place: —

$$2\ KI + MnO_2 + 2\ H_2SO_4 = MnSO_4 + K_2SO_4 + 2\ H_2O + I_2.$$

Iodine can also be displaced from iodides by means of chlorine. When a solution of potassium iodide is treated with chlorine water, the following reaction takes place: —

$$\overset{+}{K}, \overset{-}{I} + Cl = \overset{+}{K}, \overset{-}{Cl} + I.$$

This is analogous to the action of chlorine upon bromides, which we have seen consists in a transferrence of the electrical charge from the bromine ion to the chlorine. Here we have the charge transferred from the iodine ion to the chlorine, which becomes an ion, the iodine having lost its charge becoming an atom.

Chemical Properties of Iodine. — The purplish black solid, iodine, resembles strongly in its chemical properties the elements chlorine and bromine. It combines with many other elements, but is not quite as active chemically as bromine and chlorine. Iodine forms a characteristic blue color with starch paste, which enables its presence to be easily detected.

If the iodine is combined as in an iodide, it can be detected by simply adding concentrated sulphuric acid. The hydriodic acid set free reacts with the sulphuric acid, reducing it, and the iodine is liberated as such. It can be recognized by the characteristic dark brown color which it imparts to the solution.

Physical Properties of Iodine. — Although iodine is a solid at ordinary temperatures, it can readily be converted into vapor at a slightly elevated temperature. When iodine is heated exposed to the air, *i.e.* under ordinary conditions, it does not melt, but passes at once into vapor. It can, however, be melted at 114°, and boils at about 185°.

The vapor of iodine can be readily condensed to a solid when the temperature of the vapor is again lowered. This process of converting a solid into a vapor, and recondensing the vapor to a solid, is known as *sublimation.*

Iodine dissolves in water to only a slight extent. If to the water potassium iodide or hydriodic acid is added, the solution dissolves iodine in considerable quantities. Iodine dissolves readily in carbon bisulphide, chloroform, alcohol, and ether. Solutions of iodine in the last two solvents are known as *tincture of iodine.*

Hydriodic Acid, HI. — When a mixture of hydrogen and iodine is heated, there is partial combination between the two, forming hydriodic acid, HI. Only a portion of the mixture, however, combines. The *velocity of the reaction, i.e.* the amount of hydriodic acid which is formed in a given time, can be greatly increased by heating the mixture in the presence of finely divided platinum, which acts by contact, or *catalytically,* as we say. Even under these conditions a complete combination of the two gases cannot be effected.

A far more convenient method of preparing hydriodic acid is by the action of water on phosphorus triiodide, PI_3: —

$$PI_3 + 3\ H_2O = H_3PO_3 + 3\ HI.$$

Hydriodic acid cannot be prepared by the action of sulphuric acid on iodides, since, as we have seen, hydriodic acid reduces sulphuric acid. The extent to which this reduction takes place depends largely upon the temperature and concentration of the solutions, hydrogen sulphide being usually formed: —

$$2\ KI + H_2SO_4 = K_2SO_4 + 2\ HI;$$
$$H_2SO_4 + 8\ HI = 4\ H_2O + 8\ I + H_2S.$$

Compounds of Iodine with Oxygen and Hydrogen. — Iodine forms two well-characterized compounds with oxygen and hydrogen. These are *iodic acid* and *periodic acid.* When iodine is dissolved in caustic potash, the reaction takes place thus: —

$$6\ KOH + 6\ I = 5\ KI + KIO_3' + 3\ H_2O.$$

The iodates are more readily prepared by the action of iodine on chlorates. When no water is present, we have: —

$$2\ KClO_3 + 2\ I = 2\ KIO_3 + Cl_2.$$

Periodic acid does not have a composition strictly analogous to perchloric or perbromic acid, but this plus two molecules of water: —

$$\underset{\text{(unknown)}}{HIO_4} + 2\ H_2O = H_5IO_6.$$

FLUORINE (At. Wt. = 19.05)

Occurrence and Preparation. — Fluorine, on account of its unusual chemical activity, does not occur in nature in the free condition. It occurs mainly in combination with the element calcium as *fluor-spar*, from which it derives its name. Fluor-spar is so called because it readily melts and flows, serving as a flux for other substances. Fluorine also occurs in another mineral, *cryolite*, in considerable quantity. Cryolite is a

double fluoride of sodium and aluminium, occurring mainly in Greenland, and having the composition Na_3AlF_6.

The problem of isolating fluorine remained for a long time unsolved. On account of the great chemical activity of this substance, as soon as it was set free from its compounds it

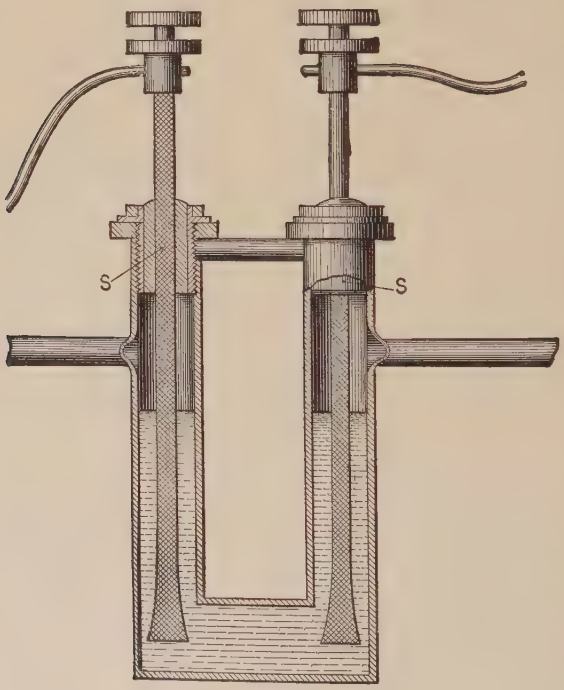

Fig. 36.

would combine again with whatever it came in contact. The problem of isolating fluorine was solved by the French chemist, Moissan.

He found that when potassium fluoride is dissolved in anhydrous hydrofluoric acid the solution conducts the current, hydrogen being liberated at the cathode and fluorine at the anode. At first the attempt was made to use vessels lined

with calcium fluoride where the fluorine escapes, but vessels of platinum were subsequently employed and found to work very satisfactorily. Indeed, it has subsequently been shown that fluorine does not act very vigorously upon copper, and copper vessels have been used in which to liberate the element fluorine.

The apparatus used by Moissan for preparing fluorine is shown in Figure 36. The apparatus and electrodes, made of platinum-iridium, have the form shown in the figure. The electrodes are insulated by means of stoppers (S.S.) of fluorspar. The apparatus is kept at a temperature of $-23°$ by means of methyl chloride. The fluorine, liberated on the anode, passes out through a spiral platinum tube cooled to $-50°$ by means of methyl chloride, and then through two tubes of sodium fluoride to remove all traces of hydrofluoric acid.

Chemical Properties of Fluorine. — Fluorine is one of the most active chemically of all the elements. It replaces chlorine from chlorides and from hydrochloric acid. At ordinary temperatures it combines with most of the metals, converting them into fluorides. Platinum and gold are about the only metals which resist its action, and these are transformed into fluorides at elevated temperatures. About the only elements which resist the action of fluorine are nitrogen, chlorine, oxygen, and argon and its associates.

Physical Properties of Fluorine. — Fluorine is a gas at all ordinary temperatures, having a light, greenish yellow color. It is much lighter in color than chlorine, and much more active upon the mucous membrane of the nose and throat.

Fluorine has been liquefied by the combined efforts of Moissan in France and Dewar in England. The fluorine was cooled to $-190°$ by means of liquid air, when it liquefied, and was received in a glass bulb with a vacuum-jacket. Fluorine boils at $-187°$, and at this low temperature has lost much of its chemical activity, as is obvious from the fact that it can be received in a glass vessel. Fluorine has recently been solidified.

Hydrofluoric Acid, HF. — Hydrogen fluoride, or hydrofluoric acid, is prepared most conveniently by the action of sulphuric acid on calcium fluoride: —

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\,HF.$$

The most characteristic chemical property of hydrofluoric acid is its power to act upon glass, etching it, as we say. It is extensively used for this purpose in preparing measuring apparatus especially for chemical work. Hydrofluoric acid does not act upon paraffine and similar organic substances. The glass vessel upon which it is desired to make a permanent line is covered with paraffine by dipping it into the molten material. A fine line is then drawn through the paraffine at the place where it is to appear on the glass. The glass is thus exposed at this place. It is now subjected to the action of the fumes of hydrofluoric acid. Where the glass is protected by the paraffine, it is not acted upon by the fumes of the acid. Where the paraffine has been removed, however, the glass is etched.

Comparison of the Several Acids formed by the Halogens. — We have seen that chlorine, bromine, iodine, and fluorine all form compounds with hydrogen which are acid. Taking these in the order of the increasing atomic weight of the halogen, we have seen that hydrofluoric acid is the most stable of all the compounds of the halogens with hydrogen. Hydrochloric acid is next, and this is followed in the order of decreasing stability by hydrobromic and hydriodic acids. Indeed, the last-named substance is quite unstable. Of the four acids; hydrochloric, hydrobromic, and hydriodic are of about equal strength, and are among the strongest acids, while hydrofluoric acid is a much weaker acid.

If we turn to the compounds with oxygen and hydrogen, we find the order exactly reversed. Fluorine forms no known compound with oxygen. Chlorine forms very unstable compounds with hydrogen and oxygen, bromine more stable compounds, while iodine forms fairly stable substances when combined with oxygen and hydrogen.

EXPERIMENTS WITH BROMINE, IODINE, AND FLUORINE

Experiment 73. Preparation of Bromine from Potassium Bromide, Manganese Dioxide, and Sulphuric Acid.—(Retort holding 500 cc.; receiver; evaporating-dish large enough to hold the receiver; potassium bromide; manganese dioxide; sulphuric acid concentrated; ice.)

(All experiments with bromine, iodine, and fluorine must be carried out under the hood.)

Place the receiver in the evaporating-dish containing ice-water. Support the retort on an iron stand as in Figure 3. Mix 4 grams potassium bromide with 8 grams manganese dioxide, and introduce the mixture into the retort. Add slowly 18 cc. of concentrated sulphuric acid to 100 cc. of water. When cold introduce the mixture into the retort. Insert the arm of the retort into the neck of the receiver and heat slowly the contents of the retort. The bromine will condense in the receiver as a dark reddish liquid.

Write equations for above reactions? (See page 133.)

Experiment 74. Solidification of Bromine.—(Test-tube; evaporating-dish; mixture of finely powdered ice and salt.)

Introduce a few centimetres of bromine into a small test-tube and plunge the tube into a mixture of finely powdered ice and salt. The bromine freezes, forming a yellowish red solid. (See page 135.)

Experiment 75. Preparation of Bromine Water. — (Erlenmeyer flask holding 300 cc.; cork; bromine.)

Introduce into the flask 150 cc. of water; add 2 cc. of bromine. Cork the flask and shake carefully from time to time. The bromine gradually dissolves, forming a yellowish solution known as *bromine water*. Is chlorine soluble in water? How is chlorine water made? (See page 135.)

Experiment 76. Action of Bromine on Other Elements. — (Beaker; test-tube; bromine; arsenic.)

Into a small test-tube introduce a few cubic centimetres of bromine. Great care must be taken not to allow bromine to come in contact with the hand, or very painful wounds will result.

Place the test-tube in the beaker. If the test-tube should break, the beaker will catch the bromine and prevent it damaging the floor of the hood.

Introduce a piece of arsenic or antimony the size of a grain of rice. Vigorous chemical reaction takes place; the arsenic or antimony becomes red-hot.

Does chlorine act on arsenic or antimony? (See page 134.)

Experiment 77. Preparation of Hydrobromic Acid by the Action of Sulphuric Acid on Potassium Bromide. — (*This experiment to be performed by the instructor.*) (Thistle-tube; Florence or balloon flask 500 cc.; U-tube; funnel; beaker; red phosphorus; potassium bromide; sulphuric acid.)

Arrange an apparatus as shown in Figure 37. Fifteen grams of potassium bromide are introduced into the flask *A*. The U-tube is filled with a mixture of red phosphorus and fragments of glass. The red phosphorus removes any bromine from the

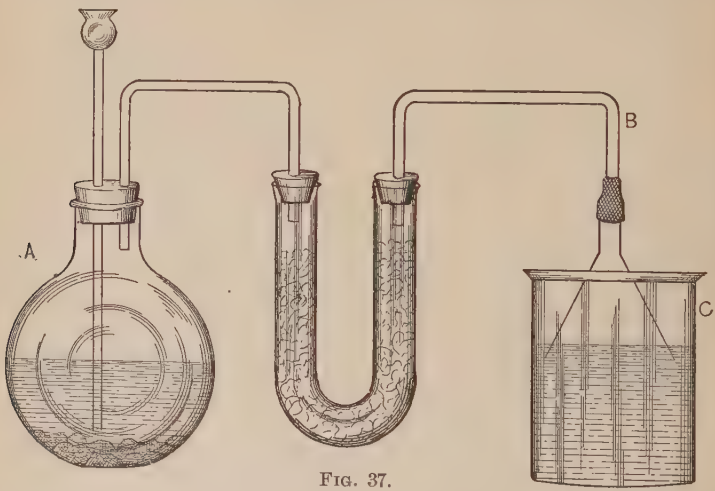

Fig. 37.

gas, and the fragments of glass prevent the tube from being closed by the red phosphorus. A funnel is attached to the end of the tube *B*, and dips just beneath the surface of the water in the beaker *C*.

Add 75 cc. of concentrated sulphuric acid very slowly to 25 cc. water. When the mixture is cold, pour into the flask through the thistle-tube enough of the mixture to cover the solid potassium bromide. Carefully warm the flask. Hydrobromic acid will be evolved, and will be readily absorbed by the water in the beaker.

Continue the experiment until considerable gas has been dissolved in the water. Preserve this solution for the following experiment.

Write the equations for the above reactions?

Write the equations when potassium bromide is treated with concentrated sulphuric acid?

Test the action of concentrated sulphuric acid on a crystal of potassium bromide? (See page 135.)

Experiment 78. Properties of Hydrobromic Acid. — (Test-tubes; red litmus paper; potassium hydroxide; chlorine water; solution of hydrobromic acid.)

Pour a little aqueous hydrobromic acid into a test-tube; add a drop of litmus or dip into the solution a strip of blue litmus paper. Observe what change takes place in the litmus. Explain?

Neutralize another portion of the solution of hydrobromic acid with potassium hydroxide. Evaporate the solution to dryness on the water-bath. What is the substance obtained?

To the aqueous solution of hydrobromic acid add a little chlorine water. The solution turns reddish brown. Explain the change in color? (See page 135.)

Experiment 79. Detection of Bromine in Bromides, and when in the Presence of Chlorine. — (Potassium bromide; potassium chloride; chlorine water; carbon bisulphide; silver nitrate; ammonia.)

Prepare a solution of a few crystals of potassium bromide. Add a few cubic centimetres of carbon bisulphide, which being heavier than the solution settles at once to the bottom of the test-tube. Add chlorine water drop by drop, shaking vigorously after the addition of each drop. The bromine set free by the chlorine will be dissolved by the carbon bisulphide, and will impart to it its characteristic red color.

Treat a dilute solution of potassium bromide with a dilute solution of silver nitrate. White silver bromide will be precipitated. Equation? Add a *few drops* of dilute ammonia, and the white precipitate does not dissolve. Compare this with the solubility of silver chloride in ammonia?

Mix a gram of potassium bromide with a gram of potassium chloride, and dissolve the mixture. To a part of the mixture in a test-tube add a little carbon bisulphide and then add chlorine water drop by drop, shaking the solution vigorously after the addition of each drop. The chlorine liberates the bromine, which gives its characteristic color to the carbon bisulphide.

Treat another portion of the solution with the solution of silver nitrate until all of the bromine and chlorine have been

precipitated as the silver salts. Add a *few drops* of dilute ammonia. The ammonia will dissolve a part of the silver chloride, but leave undissolved the silver bromide. Filter the solution from the undissolved solid, and add to the clear filtrate a little nitric acid. Silver chloride will be precipitated. Thus we detect a chloride and a bromide in the presence of each other. (See page 134.)

Experiment 80. Preparation of Iodine from Potassium Iodide, Manganese Dioxide and Sulphuric Acid. — (Retort holding 300 cc.; receiver; potassium iodide; manganese dioxide; sulphuric acid.)

Arrange an apparatus as in Figure 32, omitting the cooling agent around the receiver. Mix 5 grams of potassium iodide and 10 grams of finely powdered manganese dioxide. Introduce the mixture into the retort. Add 15 cc. of concentrated sulphuric acid to 85 cc. water; allow the mixture to cool, and introduce into the retort. Heat gently. Vapors of iodine will fill the retort and condense on its walls and in the receiver. (See page 137.)

Experiment 81. Properties of Iodine; Action on Phosphorus and Zinc. — (Porcelain crucible; iodine; phosphorus; zinc dust.)

Bring a few crystals of iodine into a porcelain crucible. Dry a piece of phosphorus the size of a pea by pressing it between layers of filter-paper, and throw it into the crucible in contact with the iodine. Vigorous chemical reaction will quickly take place.

Mix in a crucible 4 grams of iodine which has been finely powdered, with 1 gram of zinc dust. Add a drop or two of water. Chemical reaction will take place. (See page 138.)

Experiment 82. Properties of Iodine — Sublimation; Solubility; Reaction with Starch. — (500 cc. flask; carbon bisulphide; potassium iodide; iodine; starch.)

Introduce a few grams of iodine into a flask holding 500 cc. Place the flask on a sand-bath or an asbestos board, having wrapped a piece of filter-paper, moistened with cold water, around the top and neck of the flask. The iodine volatilizes without melting, and crystallizes on the walls of the flask in beautiful plate-like crystals.

While iodine is only slightly soluble in water, it dissolves readily in carbon bisulphide. Shake a crystal of iodine with a few cubic centimetres of carbon bisulphide, and note the color of the solution?

Add a few crystals of iodine to an aqueous solution of potas-

sium iodide. It readily dissolves, forming "tincture of iodine." Note the color?

Prepare a little starch-paste as follows: Place a few granules of starch in a mortar and add enough cold water to just moisten the starch. Grind the starch to a paste with the pestle. Pour the starch into a beaker containing hot (but not boiling) water. It is then ready for use.

Fill a test-tube about one-third full with the starch-paste. To one drop of the solution of iodine in potassium iodide add 20 cc. of water. Add a few drops of this very dilute solution of iodine to the starch-paste. A deep blue color at once appears. This is a very sensitive reaction for iodine. (See page 138.)

Experiment 83. Action of Sulphuric Acid on Potassium Iodide. — (A few crystals of potassium iodide; concentrated sulphuric acid.)

Dissolve a few crystals of potassium iodide in a little water in a test-tube, and add a few drops of concentrated sulphuric acid. We would expect that under these conditions hydriodic acid would be liberated. The hydriodic acid, however, acts as a reducing agent, and we have iodine set free in the solution. The hydrogen of the hydriodic acids reacts with more sulphuric acid, reducing it to sulphur dioxide, sulphur, or hydrogen sulphide; depending upon the strength of the solution of the acid used, and upon the temperature. Carefully smell the gases escaping from the test-tube? (See page 139.)

Experiment 84. Detection of Iodine. — (Potassium iodide; carbon bisulphide; chlorine water; silver nitrate; ammonia.)

Dissolve a few crystals of potassium iodide in water; add a solution of silver nitrate. A *yellow* precipitate is formed, which is insoluble in ammonia; thus differing from silver chloride, which is readily soluble in ammonia, and from silver bromide, which is soluble in a large volume of ammonia. To a solution of potassium iodide add chlorine water, drop by drop, having previously added a little carbon bisulphide. The whole is shaken vigorously. The carbon bisulphide acquires the characteristic purplish color which is produced by iodine. (See page 138.)

Experiment 85. Detection of Iodine in the Presence of Chlorine and Bromine. — (Potassium iodide; potassium bromide; potassium chloride; carbon bisulphide; chlorine water; silver nitrate; ammonia.)

Mix 1 gram of potassium iodide, 1 gram of potassium bromide, and 1 gram of potassium chloride, and dissolve the mix-

ture in 50 cc. of water. To a portion of the solution add silver nitrate until all of the iodine, bromine, and chlorine are precipitated as the corresponding silver compounds. Add a little dilute ammonia, filter, and the chlorine will be in the filtrate; explain? Add a little nitric acid to the filtrate, and silver chloride will be reprecipitated.

Add an excess of ammonia to the mixture of silver bromide and iodide, and the bromide will dissolve, leaving the yellow silver iodide behind, since the latter is insoluble in ammonia. Again filter, and the bromine will be in the filtrate. Add a little nitric acid to the filtrate, and silver bromide will be reprecipitated. The insoluble silver iodide will remain on the filter-paper. The above is a rough qualitative method for separating the three halogens, — chlorine, bromine, and iodine.

A much simpler method of detecting iodine in the presence of bromine and chlorine is the following: To a little of the solution of the above mixture add a few cubic centimetres of carbon bisulphide, and then add chlorine water, drop by drop, shaking vigorously. The iodine separates first, and its presence is detected by the purple color which it imparts to the carbon bisulphide. More chlorine water causes this color to disappear, since the iodine is oxidized to iodic acid, which is colorless. Further addition of chlorine water throws out the bromine, which gives a dull red color to the carbon bisulphide. This color persists on further addition of chlorine water, since bromine is not oxidized by this reagent.

Experiment 86. Preparation of Hydrofluoric Acid; Etching Glass. — (Platinum or lead dish; powdered fluor-spar; concentrated sulphuric acid; glass plate; paraffine.)

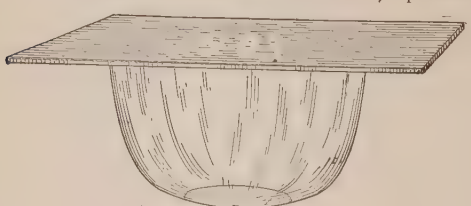

Fig. 38.

Concentrated sulphuric acid is added to finely powdered fluor-spar until the mass has the consistency of paste. Over the dish is placed a glass plate covered with paraffine (by dipping it into molten paraffine), and containing a few lines or characters drawn in the paraffine (Fig. 38). The whole is now set in a warm place and allowed to remain for some hours. Where the lines were drawn the paraffine was removed, and the glass ex-

posed to the fumes of the hydrofluoric acid set free by the action of sulphuric acid on calcium fluoride. Remove the paraffine by dissolving it in warm turpentine, and the design will be permanently etched upon the glass. Lines are thus etched upon measuring apparatus. (See page 142.)

PROBLEMS

1. Weight of bromine that can be obtained from 1 kilogram of potassium bromide? With what weight of arsenic will this combine to form arsenic tribromide?

2 How much potassium bromide would be required to yield 500 grams of hydrobromic acid?

3. Ten litres of chlorine will liberate how much bromine from potassium bromide? How much potassium bromate can be formed from this amount of bromine?

4. The iodine contained in 100 grams of potassium iodide will form with phosphorus what weight of phosphorus triiodide?

5. How many grams of potassium iodide can be obtained from the iodine in 7 grams of potassium iodate?

6. When fluor-spar is decomposed by sulphuric acid, what amount is decomposed by 12 grams of the acid? What is the weight of the hydrofluoric acid liberated?

CHAPTER XV

SULPHUR, SELENIUM, TELLURIUM

SULPHUR (At. Wt. = 32.06)

Occurrence and Purification. — Sulphur occurs in great abundance in nature in the free condition. This is especially true in volcanic regions such as those of Italy, Sicily, Iceland, etc.

Sulphur also occurs in combination with a number of other elements. In combination with oxygen as sulphur dioxide, SO_2, it escapes in certain volcanic regions. Combined with hydrogen as hydrogen sulphide, H_2S, it also issues from the earth in the neighborhood of certain volcanoes. It also exists in combination with a number of metals as sulphides. We have lead sulphide or *galena*, PbS, iron sulphide or *pyrites*, FeS_2, antimony sulphide or *stibnite*, Sb_2S_3, copper iron sulphide or *copper pyrites*, $Cu_2Fe_2S_4$. The sulphur that occurs in the free condition in nature does not all escape from the interior of the earth in the form of sulphur, but is deposited as the result of the action of one sulphur compound on another, or of oxygen on hydrogen sulphide: —

$$2\,H_2S + O_2 = 2\,H_2O + 2\,S\,;$$
$$SO_2 + 2\,H_2S = 2\,H_2O + 3\,S.$$

Sulphur as it occurs in nature contains more or less impurities. The sulphur is freed from these by fusion. The first more or less crude product is known as *crude brimstone*. The crude brimstone is then redistilled, and either condensed in a state of fine division as *flowers of sulphur*, or the molten mass poured into moulds as *roll* or *stick sulphur*.

Chemical Properties of Sulphur. — Sulphur at ordinary temperatures is comparatively inert. Indeed, at elevated temperatures it is less active chemically than members of the halogen group at ordinary temperatures. When heated in the presence of the air sulphur combines with oxygen, forming sulphur dioxide: —

$$S + O_2 = SO_2.$$

Sulphur, however, combines with many of the elements, forming well-defined compounds of sulphur. The compounds with the metals, known as the *sulphides*, have characteristic properties which are very useful, as we shall learn, in qualitative analysis.

Physical Properties of Sulphur. — Sulphur is a yellowish solid at all ordinary temperatures, melting at 118° and boiling at 448°.4. The solid sulphur is known in two forms. If allowed to crystallize from a solution of carbon bisulphide, and as found in nature, it crystallizes in the orthorhombic system. In this system the three axes all make right angles with one another, and are all of unequal lengths.

If, on the other hand, ordinary flowers of sulphur, roll sulphur, or orthorhombic sulphur is melted and allowed to cool slowly in a hessian crucible, we obtain the sulphur in the form of needles which belong to the monoclinic system. In the monoclinic system two axes are at right angles to one another, while the third is inclined. The three axes are all of unequal lengths.

Substances which can crystallize in several systems are know as *polymorphous ;* when they crystallize in two systems, as *dimorphous.* Sulphur is, therefore, *dimorphous.* Take the two crystalline modifications of sulphur; they are obviously analogous to oxygen and ozone.

In the case of oxygen and ozone we have seen that the fundamental and important difference is in the amounts of intrinsic energy present in the molecules of the two substances. We would naturally ask whether any such difference exists between orthorhombic and monoclinic sulphur. This

can be answered very simply in the case of sulphur; indeed, more simply and directly than with oxygen and ozone. It is only necessary to burn equal quantities of the two modifications of sulphur in oxygen and measure the amounts of heat liberated.

A considerable difference was found in the amounts of heat liberated in the two cases. Thirty-two grams, or a gram-atomic weight, of orthorhombic sulphur when burned to sulphur dioxide liberated 71,000 calories of heat. An equal weight of monoclinic sulphur burned to sulphur dioxide set free 73,300 calories of heat. The difference, 2300 calories, is the thermal equivalent of the difference in the intrinsic energy of the two modifications.

Sulphur, as has been stated, melts at 118°. It first passes over into a thin, light yellow liquid, which, on further rise in temperature, passes through a remarkable series of transformations. When heated to 160° the yellow liquid passes over into a reddish brown, viscous mass, which becomes deeper brown in color and more viscous as the temperature is raised to 250°. If the temperature is still further raised until 400° is reached, the viscous mass becomes a yellow liquid again, which boils at 448°.4. When the boiling sulphur is allowed to cool, it passes through these same changes again, but in reverse order.

Hydrogen Sulphide, H_2S. — This compound occurs in nature in the free condition, as we have seen. It escapes from fissures in certain localities, and is dissolved in certain waters, producing *sulphur water*.

By far the best method of preparing hydrogen sulphide, and the one which is always employed, is to treat certain sulphides with an acid. The sulphide which it is most convenient and economical to use is ferrous sulphide, FeS. When this is treated with sulphuric or hydrochloric acid, the following reaction takes place: —

$$FeS + H_2SO_4 = FeSO_4 + H_2S,$$
$$FeS + 2\,HCl = FeCl_2 + H_2S.$$

Chemical Properties of Hydrogen Sulphide. — The most important chemical application of hydrogen sulphide is in connection with its action on the soluble salts of the heavy metals. Take as an example its action on solutions of silver nitrate: —

$$2\,AgNO_3 + H_2S = Ag_2S + 2\,HNO_3.$$

In such cases we have the sulphide of the metal precipitated with its characteristic properties.

It is generally true that when hydrogen sulphide is passed into solutions of salts of the heavy metals the sulphide of the metal is precipitated. If this does not take place otherwise, it is effected by making the solution slightly alkaline.

The sulphides of certain metals resemble one another with respect to a given property. This enables us to separate the metals into groups by means of hydrogen sulphide. The sulphides of certain metals are soluble in water.

There is another group of elements whose sulphides dissolve in dilute acids. These can be precipitated as a group, not by hydrogen sulphide, since this would necessitate the formation of free acid and the consequent solution of the sulphide, but by a soluble sulphide. The sulphide employed is ammonium sulphide, and this group of elements is known as the *ammonium sulphide group.*

There remains a group of elements whose sulphides are not soluble in cold, dilute acids. Salts of these metals are readily precipitated by hydrogen sulphide, since the acid set free does not dissolve the sulphide when formed.

This group of elements is known as the *hydrogen sulphide group.* Here again individual differences between the sulphides are utilized to separate the several members.

Hydrogen sulphide is easily oxidized in the sense of the following equation: —

$$2\,H_2S + O_2 = 2\,H_2O + 2\,S.$$

Acid Sulphides. — Hydrogen sulphide, as we have seen, has the composition H_2S, and forms salts with univalent elements

having the composition M_2S, M representing any univalent element. If M represents a bivalent element, the salt has the composition MS.

Hydrogen sulphide can also form a different class of salts in which one of the hydrogen atoms is still present. With univalent elements these would have the general composition MHS, with bivalent elements $M(HS)_2$. We have a number of examples of these *hydrosulphides* or *acid sulphides* as they are called. Ammonia forms the hydrosulphide very readily when hydrogen sulphide is conducted into aqueous ammonia: —

$$NH_3 + H_2S = NH_4HS.$$

Indeed, this is the compound which is formed when aqueous ammonia is saturated with hydrogen sulphide.

Dissociation of Hydrogen Sulphide. — The hydrosulphides or acid sulphides are, as we have seen, salts of a monobasic acid. The sulphides, on the other hand, are salts of a *dibasic acid*, *i.e.* one which combines with two univalent ions. How can we explain these facts on the basis of the dissociation theory?

There are two different ways in which hydrogen sulphide can dissociate. These are the following: —

$$H_2S = \overset{+}{H},\overset{-}{HS}, \qquad (1)$$

$$H_2S = \overset{+}{H},\overset{+}{H},\overset{=}{S}. \qquad (2)$$

When the compound dissociates as in equation (2), it is obviously dibasic; when the dissociation takes place as in equation (1), it is monobasic.

Physical Properties of Hydrogen Sulphide. — Hydrogen sulphide is a colorless gas, with an extremely disagreeable odor, suggesting decomposing organic matter. When taken into the lungs in any great quantity, it is quite poisonous. For this reason and on account of its disgusting odor it should never be allowed to escape into the air of a laboratory. Since it is so frequently used in connection with qualitative analysis, a separate room is attached to every well-equipped chemical

laboratory in which the gas is generated and used. This is known as the *sulphuretted hydrogen room.*

Hydrogen sulphide dissolves in water to the extent of from $2\frac{1}{2}$ to 3 volumes of the gas in one volume of water.

COMPOUNDS OF SULPHUR WITH OXYGEN AND HYDROGEN

Sulphur Dioxide, SO_2. — The simplest compound of sulphur and oxygen is sulphur dioxide, having the composition SO_2. It is formed by the direct combination of the two elements when sulphur is burned in oxygen: —

$$S + O_2 = SO_2.$$

A more convenient method of preparing sulphur dioxide is by the action of strong acids on sulphites, or acid sulphites. Normal sodium sulphite has the composition Na_2SO_3. When this is treated with sulphuric acid the following reaction takes place: —

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

Another very convenient method for preparing sulphur dioxide is by the action of sulphuric acid on metallic copper: —

$$Cu + 2\ H_2SO_4 = CuSO_4 + 2\ H_2O + SO_2.$$

It is a colorless gas with very penetrating odor, and a taste which persists for an unusual time. Its odor and taste are characteristic of a burning sulphur match, with which every one is familiar. It readily takes up oxygen and is, therefore, an excellent reducing agent.

Sulphurous Acid, H_2SO_3. — The acid formed when sulphur dioxide is dissolved in water yields salts having the composition M_2SO_3, where M is an univalent metal. The acid must therefore have the composition H_2SO_3, and be a dibasic acid. It can also form acid sulphites of the composition $MHSO_3$.

It has been impossible to isolate the acid H_2SO_3, since it breaks down so readily into water and sulphur dioxide: —

$$H_2SO_3 = H_2O + SO_2.$$

Dissociation of Sulphurous Acid. — Sulphurous acid is a weak acid. Being a dibasic acid, it can dissociate in two ways.

$$H_2SO_3 = \overset{+}{H}, H\overset{-}{S}O_3$$

is the first stage in the dissociation. The second stage in the dissociation, produced only in very dilute solutions since sulphurous acid is a weak acid, would then be represented thus: —

$$H\overset{-}{S}O_3 = \overset{+}{H}, \overset{=}{S}O_3.$$

Sulphur Trioxide, SO_3. — Sulphur trioxide, SO_3, is formed by gently heating *fuming sulphuric acid*. The latter is really a solution of sulphur trioxide in sulphuric acid, usually having approximately the composition $H_2S_2O_7$. When this is heated, it decomposes thus: —

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

When sulphur dioxide and oxygen are heated together, they combine and form sulphur trioxide, but only in very small quantity. If, however, the mixture of the two gases is heated in the presence of certain substances, they combine readily, forming sulphur trioxide. Such a substance is finely divided platinum. If the two gases are passed through a tube containing platinum sponge, and the tube heated, they combine very readily.

This is distinctively a *catalytic reaction, i.e.* a reaction effected by a substance which does not enter into the reaction, but acts simply by contact. The platinum in this case does not enter at all into the reaction, and a very small amount of platinum is capable of effecting a large amount of the reaction. This method of preparing sulphur trioxide has been found to be so efficient and economical that it is rapidly supplanting all others, and in the near future will probably be used almost exclusively for preparing this substance.

Sulphur trioxide is a powerful oxidizing agent, readily giving up one of its oxygen atoms and passing over into sulphur dioxide. It has an unusual attraction for water, combining with it at once on mere contact, and even causing the hydrogen and oxygen in organic compounds to combine and form water, with which it instantly combines.

Sulphur trioxide is a transparent, mobile liquid, which boils at 46°.2. It can be cooled to zero without solidifying. When further cooled it forms a white solid, which melts at 14°.8.

Sulphuric Acid, H_2SO_4. — Sulphuric acid occurs in the free condition in small quantity in certain waters on the surface of the earth. It is prepared now very largely by the method described above, — by the action of water on sulphur trioxide, —

$$SO_3 + H_2O = H_2SO_4,$$

the trioxide being easily formed by the direct union of sulphur dioxide and oxygen in the presence of finely divided platinum. At an earlier date a method was employed for effecting the oxidation of sulphur dioxide, which even to-day finds considerable application. This method is based upon the oxidation of sulphur dioxide in the presence of water, nitric acid, and air.

The sulphur dioxide produced by roasting sulphides, or heating sulphur in contact with an abundant supply of air, is conducted through a tower known as the *Glover tower*. This is filled with fire-brick, over which dilute sulphuric acid trickles. The gas is cooled, and, at the same time, the dilute sulphuric acid loses water and is concentrated.

Concentrated sulphuric acid, containing the oxides of nitrogen, is brought in contact with the more dilute sulphuric acid, when it sets free these oxides which now mix with the sulphur dioxide. Nitric acid is then introduced in the form of vapor, and also water-vapor. The mixture of gases containing sulphur dioxide, nitric acid, oxides of nitrogen, and water-vapor are conducted into a chamber lined with lead, — the so-called *leaden chamber*. In these chambers, of which there are a series, the oxidation of the sulphur dioxide to sulphur trioxide takes

place, and the union of the sulphur trioxide with water, forming sulphuric acid.

In order to avoid loss of nitric acid and oxides of nitrogen, which are expensive, the sulphuric acid formed in the leaden chambers is passed through another tower, known as the *Gay-Lussac tower*. This tower contains pieces of coke over which concentrated sulphuric acid flows. The concentrated acid takes up the oxides of nitrogen. This acid is then passed into the Glover tower, where it mixes with the more dilute sulphuric acid and gives up the oxides of nitrogen, which then oxidize more sulphur dioxide to the trioxide, and the process is thus a continuous one, — a small amount of nitric acid serving to oxidize a large amount of sulphur dioxide.

The chemical reactions which take place in the manufacture of sulphuric acid by the above method, as far as they are known, are the following: —

Nitric acid acts upon sulphur dioxide in the presence of water as follows: —

$$2\,SO_2 + 2\,HNO_3 + H_2O = 2\,H_2SO_4 + N_2O_3.$$

When the sesquioxide of nitrogen, N_2O_3, reacts with water-vapor it forms nitrous acid: —

$$N_2O_3 + H_2O = 2\,HNO_2.$$

When nitrous acid reacts with sulphur dioxide in the presence of the oxygen of the air, we have: —

$$2\,SO_2 + 2\,HNO_2 + O_2 = 2\,NO_2.SO_3H.$$

The compound $NO_2.SO_3H$ is known as *nitrosyl-sulphuric acid*, or *nitrosulphonic acid*. When this is treated with water, the following decomposition takes place: —

$$NO_2.\,SO_3H + H_2O = H_2SO_4 + HNO_2.$$

The HNO_2, or its anhydride, N_2O_3, then reacts with more sulphur dioxide and oxygen and forms again NO_2, SO_3H, which then decomposes with water-vapor in the sense of the last equation, and the process is continuous; the nitrous acid or sesqui-

oxides of nitrogen being collected in the Gay-Lussac tower, as we have seen.

The acid obtained from the leaden chambers is known as *chamber acid.* It contains about 65 per cent of the compound H_2SO_4. In order to further concentrate this acid it is allowed to flow through hot, shallow, lead pans, and when the acid has become sufficiently concentrated to act chemically upon the lead, it is transferred to a platinum vessel and more of the water distilled off. The acid can be still further concentrated in vessels of platinum.

Chemical Properties of Sulphuric Acid. — One of the most characteristic properties of sulphuric acid is its power to take up water and combine with it. For this reason it is an excellent drying agent, readily taking water from other substances. When we wish to dry a gas which contains water-vapor, the best method with one exception is to allow the gas to stream slowly in fine bubbles through concentrated sulphuric acid. Its power to combine with water is the key to many of the reactions which concentrated sulphuric acid can effect. When brought in contact with many organic substances, it causes the hydrogen and oxygen to combine and form water with which it itself combines. This is the explanation of the charring of wood and similar substances effected by the concentrated acid.

Sulphuric acid has the power of driving more volatile acids out of their salts, combining with the metal of the salt. Thus, when a dry chloride or nitrate is treated with sulphuric acid, the hydrochloric or nitric acid is driven out and the sulphate of the metal is formed: —

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl;$$
$$2\,NaNO_3 + H_2SO_4 = Na_2SO_4 + 2\,HNO_3.$$

This might seem to argue that sulphuric acid was a stronger acid than either hydrochloric or nitric. Such, however, is not the case. Hydrochloric and nitric acids being volatile are displaced by much weaker, non-volatile acids, in accordance with

the general principle that *whenever a volatile compound can be formed and escape from the field of action, it is formed.*

Sulphuric acid combines with most of the metals or base-forming elements, forming sulphates. In all of these compounds the sulphuric acid is dibasic, combining with two atoms of a univalent metal, with one atom of a bivalent metal, and so on. The sulphates are stable, well-crystallized compounds. The sulphates of the heavy metals are generally only slightly soluble in water. The insolubility of its barium salt even in dilute acids furnishes us with a means of detecting sulphuric acid and determining it quantitatively.

Dissociation of Sulphuric Acid. — Sulphuric acid is a typical dibasic acid, forming two well-defined classes of salts — the *normal sulphates* and the *acid sulphates.* The former have the composition M_2SO_4 and the latter $MHSO_4$.

Like dibasic acids in general sulphuric acid dissociates in two stages. At first it breaks down, thus : —

$$H_2SO_4 = \overset{+}{H}, \overset{-}{HSO_4}.$$

When the dilution of the solution is increased, *i.e.* when more water is added, the ion $\overset{-}{HSO_4}$ dissociates thus : —

$$\overset{-}{HSO_4} = \overset{+}{H}, \overset{=}{SO_4}.$$

Sulphuric acid is a strong dibasic acid, and, therefore, the ion $\overset{-}{HSO_4}$ dissociates into $\overset{+}{H}$ and $\overset{=}{SO_4}$ before any very great dilution is reached.

Physical Properties of Sulphuric Acid. — Sulphuric acid, or oil of vitriol, is, as its name implies, a liquid. It is a thick, oily liquid, with a specific gravity of 1.84. It boils at 338°.

Scientific and Technical Uses of Sulphuric Acid. — Sulphuric acid is used very frequently in the scientific laboratory, and far more frequently in technical processes than any other acid. In scientific operations it is used as a dehydrating agent, as a drying agent to liberate volatile acids from their compounds, and in many other processes. In the arts it is used on every

hand, and crude sulphuric acid is manufactured by the hundreds of thousands of tons annually. It is used to render normal phosphates soluble in water by converting them into acid phosphates, which can be assimilated by plants. These are the basis of most of the commercial fertilizers. It is also used in connection with the manufacture of chlorine from sodium chloride, and in the preparation of soda.

Sulphuric acid is at present extensively used in connection with the generation of electrical energy in *accumulators* or *storage cells*. In such cells the electrodes are plates of lead, and the electrolyte dilute sulphuric acid.

Other Compounds of Sulphur with Oxygen and Hydrogen. — The two acids already considered, sulphurous and sulphuric, are the most important compounds of sulphur with oxygen and hydrogen. Several other compounds of sulphur with oxygen and hydrogen are known.

The *sodium salt of thiosulphuric acid* is of interest in connection with photography. It is frequently known in the arts as *hyposulphite* or simply as *hypo*. Its solution dissolves the halogen salts of silver, and it is, therefore, used for "fixing" photographs. It is formed by boiling sodium sulphite with sulphur: —

$$Na_2SO_3 + S = Na_2S_2O_3.$$

SELENIUM (At. Wt. = 79.2)

Selenium. — Selenium occurs in the same general associations as sulphur, and frequently along with sulphur. It occurs in combination with silver and copper as definite minerals. It is frequently found in the dust of flues where sulphides are roasted, or in the chambers in the manufacture of sulphuric acid. Selenium combines directly with hydrogen, forming the compound H_2Se, — *hydrogen selenide*, — which is strictly analogous to hydrogen sulphide.

Selenium combines with oxygen, forming *selenium dioxide*, the analogue of sulphur dioxide.

Selenious acid, formed by the union of selenium dioxide with water, —

$$SeO_2 + H_2O = H_2SeO_3,$$

resembles in many respects sulphurous acid.

While the compound, selenium trioxide, is not known, the acid corresponding to this anhydride is known. When selenium is treated with strong oxidizing agents, *selenic acid* or its salt is formed.

TELLURIUM (At. Wt. = 127.6)

Tellurium. — Tellurium is a much rarer element than selenium. Tellurium combines with hydrogen, forming *hydrogen telluride*, having the composition H_2Te. This is analogous to hydrogen sulphide and hydrogen selenide. It is a gas with a very disagreeable odor, like the former compounds.

Tellurium *combines with oxygen*, forming the compounds TeO, TeO_2, and TeO_3. The last two are analogous to sulphur dioxide and sulphur trioxide, while the first has no analogue among the sulphur compounds.

Tellurium, however, forms two acids with hydrogen and oxygen. These are *tellurious* and *telluric acids*, having the compositions respectively H_2TeO_3 and H_2TeO_4.

EXPERIMENTS WITH SULPHUR, SELENIUM, AND TELLURIUM

Experiment 87. Fusion and Distillation of Sulphur. — (Retort; roll sulphur; beaker filled with water.)

Arrange the retort as shown in Figure 39. Add sulphur to a retort holding 150 cc. until it is about one-fourth full. Heat slowly. The sulphur melts, forming a light yellow liquid. Continue to raise the temperature, and the liquid will become darker in color and more viscous. Heat to a still higher temperature, and the sulphur will boil and pass out of the retort in the form of vapor, or condense as a liquid in the neck of the retort.

If the liquid sulphur is allowed to run into a beaker containing cold water, it forms a tough, plastic solid, which is more or less elastic. This differs fundamentally from ordinary solid sulphur. (See page 151.)

Experiment 88. Different Crystal Forms of Sulphur. — (Erlenmeyer flask 250 cc.; roll sulphur; carbon bisulphide; porcelain or sand crucible.)

Add 400 cc. of carbon bisulphide to the Erlenmeyer flask, and then add 25 grams of sulphur. Cork the flask and shake vigorously from time to time for an hour or two. Allow the flask to stand quietly until the solution becomes clear. Pour off the clear solution into an evaporating-dish and allow the carbon bisulphide to evaporate spontaneously. Crystals of sulphur will be obtained having a given crystal form? These crystals are stable, *i.e.* do not undergo any change if allowed to stand for any length of time.

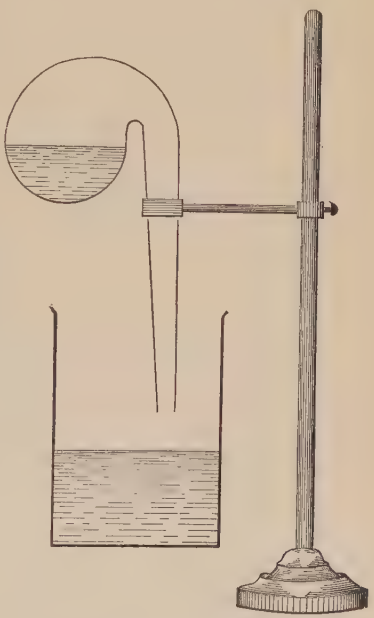

Fig. 39.

A porcelain or sand crucible holding not less than 100 cc. is filled half full of roll sulphur. The sulphur is completely melted and the crucible then covered and placed in sand in which it cools slowly. When a crust has formed on the surface, this is punctured and the molten sulphur poured out of the crucible. The walls of the crucible will be covered with fine needles, which may extend well into the crucible. *Do not touch the needles with the hand*, but remove a few of them carefully with a porcelain spatula. Compare these with sulphur crystals obtained from the carbon bisulphide. What difference in color, transparency, and form do you note?

Set some of the crystals aside for a day or two and examine them again. They are markedly changed. What changes do you note?

This form of sulphur, known as monoclinic sulphur, is unstable at ordinary temperatures and passes over into the orthorhombic form, which is the form obtained from the carbon bisulphide. (See page 151.)

Experiment 89. Reaction of Sulphur with Metals. — (Zinc dust; copper foil or copper gauze; iron powder; silver coin; sulphur.)

Mix 1 gram of sulphur with 2 grams of zinc powder, and introduce the mixture into a hot porcelain crucible or metal dish. What evidence have you of chemical action? Treat the product with hydrochloric acid and smell the escaping gas. Treat some of the unheated mixture with hydrochloric acid and smell the gas which escapes. Do the two have the same odor? Explain?

Melt a few grams of sulphur in a large test-tube and heat the sulphur to boiling. Introduce into the boiling sulphur small pieces of copper foil or copper gauze. What evidence is there of chemical action? Examine the copper strip when cold. Has any change occurred?

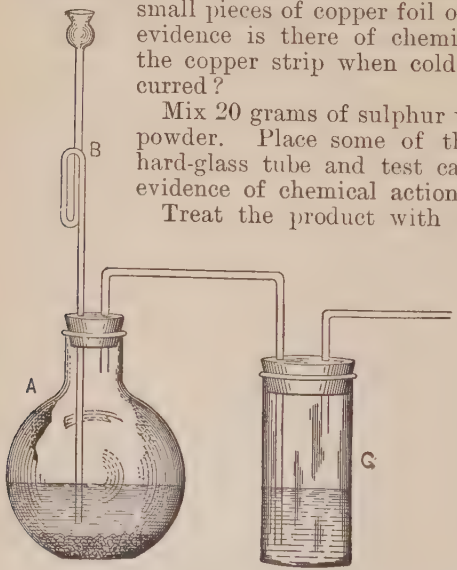

Fig. 40.

Mix 20 grams of sulphur with 10 grams of iron powder. Place some of the mixture in a large hard-glass tube and test carefully. Is there any evidence of chemical action?

Treat the product with an acid and smell the escaping gases.

Put sulphur on a moist silver coin. Does any change take place? (See page 151.)

Experiment 90. Preparation of Hydrogen Sulphide. — (Florence or balloon flask holding 500 cc.; thistle-tube; two-hole stopper; glass tubing; glass cylinder closed by a two-hole stopper; ferrous sulphide; dilute hydrochloric acid.)

Set up the apparatus as in Figure 40. Cover the bottom of the flask *A* with pieces of ferrous sulphide and add dilute hydro-

chloric acid through the thistle-tube *B*. The gas is passed through water in the cylinder *C*, and can then be passed into water giving a solution of hydrogen sulphide, or collected in cylinders by displacement of air. Since hydrogen sulphide is much heavier than air, the cylinder which is to receive the gas must be placed with its mouth upwards.

On account of the disagreeable odor and poisonous properties of hydrogen sulphide, all experiments with this gas must be performed under the hood. (See page 152.)

Experiment 91. Hydrogen Sulphide burns in Contact with the Air. — (Tall cylinder or bottle filled with hydrogen sulphide; a taper.)

Lower a lighted taper slowly into a cylinder or bottle filled with hydrogen sulphide. The taper will be extinguished, showing that hydrogen sulphide will not support combustion. The hydrogen sulphide, however, will take fire and burn at the mouth of the vessel. The combustion will not be complete, and sulphur will be deposited on the walls of the vessel. (See page 153.)

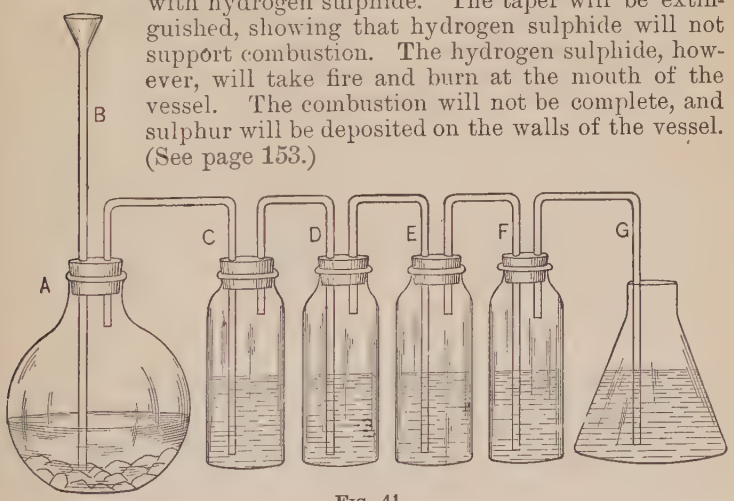

Fig. 41.

Experiment 92. Action of Hydrogen Sulphide on Salts of Metals. — (Balloon flask with a long entrance-tube; four cylinders each fitted with a two-hole rubber stopper; Erlenmeyer flask holding 250 cc.; glass tubing; ferrous sulphide; dilute hydrochloric acid; zinc sulphate; lead nitrate; cadmium chloride; antimonious chloride.)

Set up the apparatus as in Figure 41. If a Kipp apparatus for generating hydrogen is available, it may be used instead of the balloon flask. The tube *B* must be about 40 cm. long.

Introduce pieces of ferrous sulphide into A; a dilute solution of zinc sulphate into C; of lead nitrate into D; of cadmium chloride into E; and of antimonious chloride to which a little tartaric acid has been added into F. An alkali is added to G to catch any gas which may pass through all of the cylinders, and prevent it from escaping into the air of the hood.

Pour hydrochloric acid through B into A. The gas, hydrogen sulphide, will be evolved and pass through the solutions. As soon as all of the air is driven out, a white precipitate of zinc sulphide will begin to form in C; a black precipitate of lead sulphide will form in D. The yellow precipitate in E is cadmium sulphide; while orange-red antimony sulphide will be precipitated in F.

These are some of the most characteristic reactions of hydrogen sulphide. Nearly all of the heavy metals, as we shall see, are precipitated from solutions of their salts by hydrogen sulphide directly, or by the addition of ammonia after the solution has been saturated with hydrogen sulphide. (See page 135.)

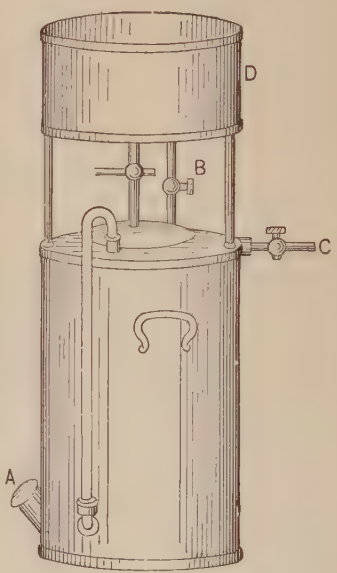

Fig. 42.

Experiment 93. Preparation of Sulphur Dioxide by burning Sulphur in Oxygen. — (Large glass tubing; porcelain boat; gasometer filled with oxygen; sulphur.) The gasometer (Fig. 42) is filled with oxygen as follows: The stop-cock C is opened. The reservoir D is filled with water and the stop-cock B opened. After filling the gasometer with water the stop-cocks C and B are closed and the cap A removed. The discharge-tube from an oxygen generating apparatus is introduced into A, and as the oxygen enters the gasometer, water escapes through A.

A hard-glass tube 20 cm. long is closed at both ends by stoppers, through which pass small glass tubes as in Figure 43. A plug of asbestos is introduced into one end of the tube, and oxygen passed through the tube until all the

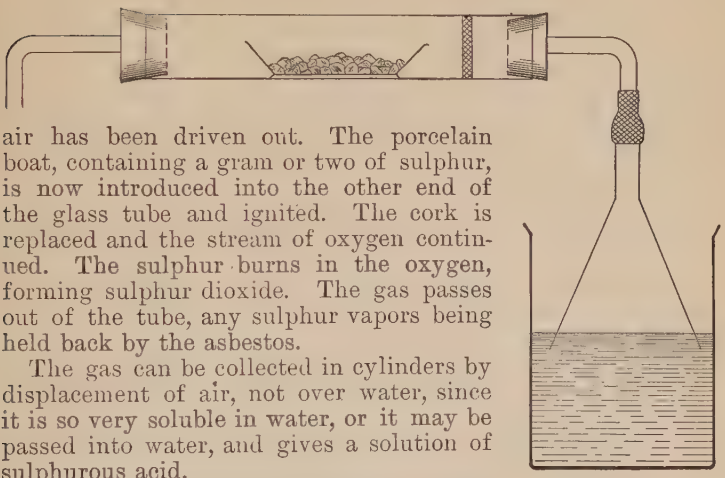

Fig. 43.

air has been driven out. The porcelain boat, containing a gram or two of sulphur, is now introduced into the other end of the glass tube and ignited. The cork is replaced and the stream of oxygen continued. The sulphur burns in the oxygen, forming sulphur dioxide. The gas passes out of the tube, any sulphur vapors being held back by the asbestos.

The gas can be collected in cylinders by displacement of air, not over water, since it is so very soluble in water, or it may be passed into water, and gives a solution of sulphurous acid.

Test the reaction of the aqueous solution towards litmus? (See page 155.)

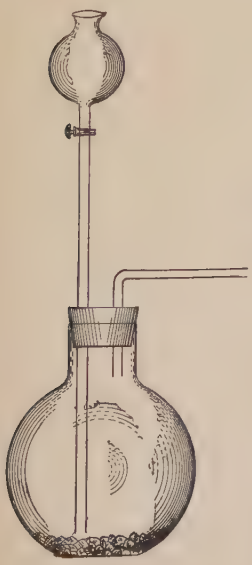

Fig. 44.

Experiment 94. Preparation of Sulphur Dioxide by the Action of Sulphuric Acid on Acid Sodium Sulphite. — (Flask holding 500 cc.; acid sodium sulphite; a mixture of one-half sulphuric acid and one-half water.)

Pour 25 grams of acid sodium sulphite into the flask (Fig. 44) and slowly drop the sulphuric acid on to the sulphite from the dropping-funnel. A steady stream of sulphur dioxide will be evolved. (See page 155.)

Experiment 95. Preparation of Sulphur Dioxide by the Action of Sulphuric Acid on Copper. — (Flask holding 500 cc.; safety-tube; discharge-tube; funnel; glass vessel.)

Arrange the apparatus as in Figure 45. Introduce some copper turnings into the flask *A*, and cover these with concentrated sulphuric acid. Warm gently, when sulphur dioxide will escape and can be dissolved in water. Sulphur

dioxide is very soluble in water, and therefore the funnel is used to prevent the return of the water into the flask *A*. (See page 155.)

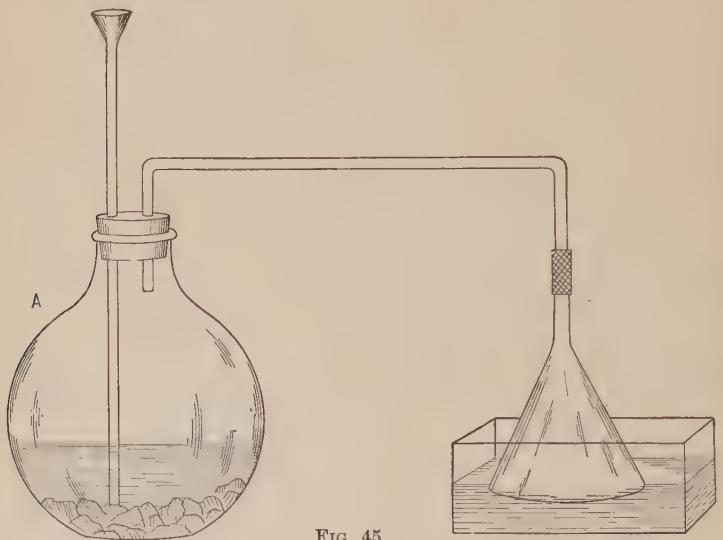

FIG. 45.

Experiment 96. Liquefaction of Sulphur Dioxide. — (Flask holding 500 cc.; dropping-funnel; gas wash-bottle; U-tube; evaporating-dish; acid sodium sulphite; sulphuric acid; salt and ice.) (*To be performed by the instructor.*)

Arrange the apparatus as in Figure 46. The acid sulphite is introduced into the flask *A*, and the mixture of equal parts of water and sulphuric acid dropped slowly on the salt. The gas is passed through sulphuric acid in the cylinder *B*, and then through the U-tube *C*, surrounded by ice and salt. The gas condenses to a liquid in the U-tube.

When liquid sulphur dioxide evaporates, which it does readily at ordinary temperatures, a low temperature is produced. Mix in a test-tube a few cubic centimetres of liquid sulphur dioxide with an equal volume of water. The water will be frozen.

Experiment 97. Bleaching Action of Moist Sulphur Dioxide. — (Bell-jar; tripod; crucible; flowers; some colored fabric; sulphur.)

Place a few grams of sulphur in the porcelain crucible. Place some flowers and a moist piece of calico fabric on the tripod

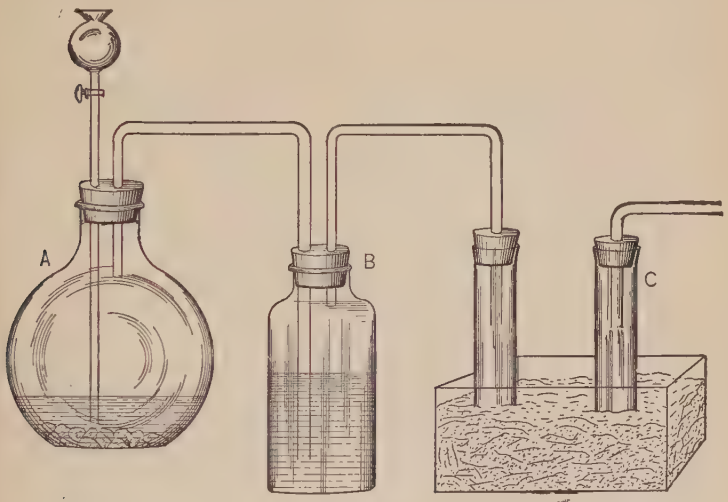

FIG. 46.

(Fig. 47). Ignite the sulphur and cover the whole with a bell-jar resting on a glass plate. In a short time the flowers and sulphur will be decolorized. (See page 155.)

Experiment 98. Reducing Action of Sulphurous Acid. — (Potassium permanganate; potassium dichromate; alcoholic solution of iodine; aqueous solution of sulphur dioxide.)

To an aqueous solution of potassium permanganate add, drop by drop, the sulphurous acid. The beautiful color of the permanganate will finally entirely disappear. Reverse the procedure, and drop the permanganate into the sulphurous acid. The disappearance of color can be readily seen.

In a similar manner add sulphurous acid to a solution of potassium dichro-

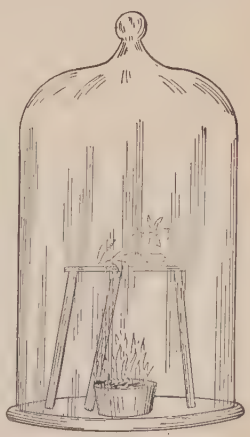

FIG. 47.

mate. The red color will disappear and a green color will be produced. Add sulphurous acid to an alcoholic solution of iodine. It will become colorless.

In all of the above reactions sulphurous acid acts as a reducing agent, it being oxidized to sulphuric acid. (See page 155.)

Experiment 99. Properties of Sulphuric Acid. — (Pine splinter; cane sugar; litmus; methyl orange; dilute sulphuric acid; concentrated sulphuric acid.)

The *power of sulphuric acid to combine with water* effects a number of chemical reactions. Introduce a pine splinter into concentrated sulphuric acid. It is quickly charred. The sulphuric acid has caused the hydrogen and oxygen in the wood to combine and form water, which it takes up, and the carbon remains behind as a black mass.

The same fact is illustrated by adding 20 grams of cane sugar to 15 cc. of hot water in a large beaker. Add 20 cc. of concentrated sulphuric acid. A vigorous reaction will take place, steam escaping, and a black carbonaceous mass will remain behind.

That *sulphuric acid is a strong acid* can be shown by adding a few drops of the dilute acid to a beaker containing 100 cc. of water and then adding a few drops of litmus. The litmus will be colored deep red.

Perform the same experiment, using methyl orange as the indicator. What do you observe? Add 10 cc. of dilute sulphuric acid to each of two beakers containing 100 cc. of water. Neutralize the acid in one beaker with sodium hydroxide, and the acid in the other beaker with potassium hydroxide, using litmus as the indicator. Evaporate the two solutions to dryness. What salts are obtained in the two cases?

Treat dry sodium chloride in a test-tube with concentrated sulphuric acid, hydrochloric acid is evolved. *This does not mean that sulphuric acid is stronger than hydrochloric acid.* Indeed, sulphuric acid is just about one-half as strong as hydrochloric acid, as has been shown by physical-chemical methods which it would lead us too far to discuss at present. *Hydrochloric acid, being volatile, is set free.* What other analogous examples have we met with? (See page 159.)

PROBLEMS

1. With what weight of sulphur would 10 litres of oxygen combine to form sulphur dioxide? to form sulphur trioxide?
2. Calculate the percentage of sulphur in ferrous sulphide?

3. With what weight of hydrogen sulphide would 5 litres of oxygen combine to form sulphur and water?

4. How much zinc sulphate, lead nitrate, and cadmium chloride would be decomposed by 1 gram of hydrogen sulphide to form ZnS, PbS, and CdS?

5. When sulphuric acid acts on 10 grams of copper, what is the weight of the sulphur dioxide set free? How much acid would be used up?

6. How much sulphuric acid could be obtained from the sulphur in 1.5 grams of pyrites?

7. Amount of ammonium hydroxide required to neutralize the above amount of sulphuric acid?

CHAPTER XVI

PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH

PHOSPHORUS (At. Wt. = 31.0)

Occurrence and Preparation. — Phosphorus derives its name from the fact that it emits light, or, as we say, is *phosphorescent*. It does not occur in the free state, but mainly in the form of phosphates, and especially in combination with calcium as the calcium salt. This is the compound of phosphorus which occurs with other substances as *apatite*, *phosphorite*, etc., and the great "phosphate beds" in the southern part of the United States are mainly calcium phosphate. Phosphorus also occurs in the bones of animals in the form of the calcium salt. Phosphorus is prepared from calcium phosphate. If bones are used as the source of the calcium phosphate, the organic matter is first destroyed by burning.

The tricalcium phosphate is treated with sulphuric acid, when *monocalcium* phosphate is formed: —

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 = 2\ CaSO_4 + Ca(H_2PO_4)_2.$$

This is then heated, when it passes over into calcium *metaphosphate*: —

$$Ca(H_2PO_4)_2 = 2\ H_2O + Ca(PO_3)_2.$$

The calcium metaphosphate is then heated with a mixture of silicon dioxide (SiO_2) and powdered charcoal. The following reaction takes place: —

$$Ca(PO_3)_2 + 5\ C + SiO_2 = 5\ CO + CaSiO_3 + 2\ P.$$

Properties of Phosphorus. — Phosphorus is a soft solid, with a slightly yellowish tint. In contact with the air it combines readily with the oxygen, forming an oxide of phosphorus.

Phosphorus combines with most of the elements, and with such elements as iodine and bromine with great vigor.

Phosphorus is an extremely poisonous substance, and in working with it precaution must be taken not to inhale its vapors.

Phosphorus exists in more than one form, there being no less than four allotropic modifications. Ordinary *yellow phosphorus* has already been briefly described.

When yellow phosphorus is allowed to stand under water for a long time, exposed to the light, it passes over into a red modification. *Red phosphorus* is easily prepared by heating the yellow phosphorus to 250° in an atmosphere free from oxygen, or to 300° in a vacuum for a few minutes. Red phosphorus is an amorphous powder, and to the eye resembles in no respect the ordinary variety. Red phosphorus is much less active chemically than yellow. When heated to 200° in the air, it does not take fire. When brought in contact with elements and compounds with which yellow phosphorus unites at once, it does not combine with them.

When red phosphorus is heated to 260° in an atmosphere of carbon dioxide, it passes over quantitatively into the yellow modification.

We have in these two varieties of phosphorus a case somewhat analogous to that met with in the two modifications of oxygen and of sulphur. We saw in the cases of oxygen and sulphur that the real difference between the properties of the two modifications was to be sought for in the different amounts of intrinsic energy present in the two modifications.

We should, therefore, naturally ask whether there is any similar relation between the two modifications of phosphorus described above? Do the different modifications contain different amounts of intrinsic energy? This can be answered by burning the different modifications in oxygen, when they yield the same end product, phosphorus pentoxide, P_2O_5. The results of thermochemical measurements show that yellow

phosphorus when burned evolves, per gram-atomic weight, 27,300 calories of heat more than red phosphorus, and this is approximately the thermochemical equivalent of the difference between the intrinsic energies of these two modifications of phosphorus.

Hydrogen Phosphide, or Phosphine, is prepared by the action of caustic potash on phosphorus in the presence of water: —

$$3\,KOH + 4\,P + 3\,H_2O = 3\,H_2KPO_2 + PH_3.$$

Phosphine produced by this method always contains a little of the liquid compound P_2H_4, which renders it spontaneously inflammable.

Compounds of Phosphorus with Oxygen and Hydrogen. — Phosphorus forms a number of compounds with oxygen. The more important are: phosphorus sesquioxide, P_2O_3, and phosphorus pentoxide, P_2O_5.

The sesquioxide of phosphorus, P_2O_3, is formed by the incomplete oxidation of phosphorus. When phosphorus is burned in a slow current of air, which does not furnish enough oxygen to convert it into the pentoxide, it forms the sesquioxide. The sesquioxide readily takes up oxygen and passes over into the pentoxide.

Phosphorus pentoxide, P_2O_5, is formed by the oxidation of phosphorus in the presence of an excess of oxygen. It is a beautifully white compound, which has remarkable power to combine with water. Indeed, it is the best drying agent at the disposal of the chemist. Phosphorus pentoxide is the anhydride of an acid. When it combines with the maximum amount of water, it forms phosphoric acid: —

$$P_2O_5 + 3\,H_2O = 2\,H_3PO_4.$$

This brings us to the acids of phosphorus, of which there are several.

The Acids of Phosphorus. — Phosphorus combines with oxygen and hydrogen, forming a number of compounds which are acids. The more important are: —

Phosphoric acid . . .	H_3PO_4
Pyrophosphoric acid . . .	$H_4P_2O_7$
Metaphosphoric acid . . .	HPO_3
Phosphorous acid	H_3PO_3

The most important of these, by far, is ordinary phosphoric acid, or orthophosphoric acid.

Orthophosphoric Acid, H_3PO_4. — Orthophosphoric acid is formed, as already stated, by dissolving phosphorus pentoxide in water. It is in the form of salts of this acid that phosphorus occurs in nature; the calcium salt, Ca_3PO_4, being the compound in which phosphorus occurs in the great phosphate beds. When this salt, which is insoluble in water, is treated with an excess of concentrated sulphuric acid, the following reaction takes place: —

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 = 3\,CaSO_4 + 2\,H_3PO_4,$$

giving free orthophosphoric acid.

The *tertiary* or *normal phosphates* have the composition M_3PO_4, where M is a univalent metal; the *secondary* phosphates, the composition HM_2PO_4; and the *primary* phosphates, the composition H_2MPO_4.

Dissociation of Phosphoric Acid. — Since phosphoric acid is a tribasic acid, it must dissociate into three hydrogen ions. The complete dissociation of phosphoric acid in the following sense is very difficult to effect: —

$$H_3PO_4 = \overset{+}{H},\ \overset{+}{H},\ \overset{+}{H},\ \overset{\equiv}{PO_4},$$

since phosphoric acid is a comparatively weak acid.

Phosphoric acid dissociates first as follows: —

$$H_3PO_4 = \overset{+}{H},\ \overset{-}{H_2PO_4}.$$

When more water is added, or when these hydrogen ions have been used up by a base, the second hydrogen begins to split off in the ionic state: —

$$\overset{-}{H_2PO_4} = \overset{+}{H},\ \overset{=}{HPO_4}.$$

It is not until these hydrogen ions have been used up, or very great dilution has been reached, that the third hydrogen ions begin to split off: —

$$\overline{\overline{HPO_4}} = \overset{+}{H}, \overline{\overline{PO_4}}.$$

Hydrolytic Dissociation. — It is a general rule that the salts of weak acids or bases are acted on by water to a greater or less extent, being broken down into the corresponding acid and base. Take tertiary, or normal sodium phosphate, Na_3PO_4. When this is acted on by water, the following decomposition takes place to some extent: —

$$Na_3PO_4 + H_2O = \overset{+}{Na}, \ \overset{+}{Na}, \ \overline{\overline{HPO_4}} + \overset{+}{Na}, \ \overline{OH}.$$

This kind of dissociation is known as *hydrolytic dissociation*. This is the explanation of the alkaline reaction shown by such compounds in water.

Pyrophosphoric Acid, $H_4P_2O_7$. — Pyrophosphoric acid is formed from phosphoric acid by loss of water: —

$$2\,H_3PO_4 = H_2O + H_4P_2O_7.$$

Salts of this acid are easily obtained by heating secondary phosphates: —

$$2\,HM_2PO_4 = H_2O + M_4P_2O_7.$$

Metaphosphoric Acid, HPO_3. — Metaphosphoric acid is formed when normal phosphoric acid is heated higher than is necessary to form the pyroacid: —

$$H_3PO_4 = H_2O + HPO_3.$$

Salts of this acid are formed when primary phosphates, MH_2PO_4, are heated: —

$$MH_2PO_4 = H_2O + MPO_3.$$

Phosphorous Acid, H_3PO_3. — Phosphorous acid is formed by the action of phosphorus on moist air. Also by the action of water on a chloride of phosphorus with which we shall soon become familiar — phosphorus trichloride: —

$$PCl_3 + 3\,H_2O = 3\,HCl + H_3PO_3.$$

Phosphorous acid contains three hydrogen atoms, and would, therefore, be expected to be a tribasic acid. The fact is, it is only dibasic, the salts richest in metal having the composition M_2HPO_3. This is to be explained as follows: The first stage in the dissociation of this substance is represented by the following equation: —

$$H_3PO_3 = \overset{+}{H},\ H_2\overset{-}{P}O_3.$$

The second stage is represented thus: —

$$H_2\overset{-}{P}O_3 = \overset{+}{H},\ H\overset{=}{P}O_3.$$

It is impossible to go farther and split off the last hydrogen atom as an ion.

COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS

Phosphorus Trichloride, PCl_3. — When chlorine gas is passed over an excess of phosphorus, in an atmosphere free from oxygen, the two combine and form phosphorus trichloride: —

$$2\,P + 3\,Cl_2 = 2\,PCl_3.$$

This compound, when brought in contact with water, decomposes, forming phosphorous acid and hydrochloric acid: —

$$PCl_3 + 3\,H_2O = 3\,HCl + H_3PO_3.$$

Phosphorus has the power to take up more chlorine and form phosphorus pentachloride.

Phosphorus Pentachloride, PCl_5. — The pentachloride of phosphorus is formed, as stated above, by the action of chlorine on the trichloride of phosphorus; also by the direct action of an excess of chlorine on phosphorus. Like the trichloride it is readily decomposed by water, forming phosphoric and hydrochloric acids: —

$$PCl_5 + 4\,H_2O = 5\,HCl + H_3PO_4.$$

ARSENIC (At. Wt. = 74.9)

Occurrence, Preparation, and Properties. — An element closely allied chemically to phosphorus is arsenic. That there are marked differences, however, will appear as the following chapter develops.

Arsenic does occur in the free condition. It is generally in combination with the metals, either directly as in the compound with iron, Fe_2As_3, or with sulphur as in *arsenical pyrites*, FeAsS.

Arsenic is generally obtained from its compounds by simply heating them; the arsenic being volatile, passes off as vapor.

Arsenic is a solid at ordinary temperatures, gray in color and very brittle.

Compound of Arsenic with Hydrogen — Arsine, AsH_3. — Arsenic forms with hydrogen the compound AsH_3, which is analogous to ammonia, NH_3. It is formed by the action of nascent hydrogen on compounds of arsenic. When we have a compound of arsenic in the presence of zinc and an acid, arsine is formed. If the compound is ordinary arsenic trioxide, As_2O_3, this is reduced by nascent hydrogen as follows: —

$$As_2O_3 + 6\,H_2 = 3\,H_2O + 2\,AsH_3.$$

When arsine is heated, it is broken down into its elements, arsenic and hydrogen. When arsine is burned and a cold object introduced into the flame, arsenic is deposited upon the object. These reactions are made use of for the detection of arsenic. *Marsh's method* for detecting arsenic consists in reducing the arsenic compound to arsine and burning the arsine.

COMPOUNDS OF ARSENIC WITH OXYGEN AND HYDROGEN

Compounds of Arsenic with Oxygen. — Arsenic forms two compounds with oxygen. One of these has the composition As_2O_3, and is known as *arsenic trioxide;* the other has the composition As_2O_5, and is known as *arsenic pentoxide.*

Arsenic Trioxide, As_2O_3, is formed when arsenic is oxidized either by burning in the air, or by some strong oxidizing agent such as nitric acid.

Arsenic Pentoxide, As_2O_5. — Arsenic pentoxide cannot be formed like phosphorus pentoxide by burning the element in oxygen. It is prepared by removing water from arsenic acid, and is, therefore, the anhydride of this acid.

Arsenious Acid, H_3AsO_3. — This acid is not known in the free condition. There are, however, three classes of salts known, depending upon whether one, two, or three of the hydrogen ions have given their electrical charges to the metal atoms which have entered the compound in their stead.

Arsenic Acid, H_3AsO_4. — When ordinary white arsenic, or arsenic trioxide, is heated with some strong oxidizing agent such as nitric acid, or aqua regia, in the presence of water, it is oxidized to arsenic acid. The reaction consists in the direct addition of oxygen and water: —

$$As_2O_3 + O_2 + 3\,H_2O = 2\,H_3AsO_4.$$

The acid is known in solution as a syrupy liquid, and in the solid form as white needles. Like phosphoric acid it forms three series of salts, — *primary*, *secondary*, and *tertiary*.

Sulpho-salts of Arsenic. — Arsenic forms with sulphur and the alkali metals, salts of acids having the composition H_3AsS_3 and H_3AsS_4. These acids are the sulphur analogues of arsenious acid, H_3AsO_3, and arsenic acid, H_3AsO_4. The *sulpho-acids* or *thioacids* are themselves not known, but certain salts are well-characterized substances.

ANTIMONY (At. Wt. 120.0)

Occurrence and Preparation. — Another element which presents many chemical analogies to phosphorus and arsenic is antimony. Antimony occurs in nature chiefly as the trisulphide, Sb_2S_3, which is known as the mineral *stibnite*. It also occurs in combination with arsenic and also with oxygen.

Antimony is prepared from stibnite by roasting out the sulphur. The sulphide is heated in the air, when the sulphur is converted into the dioxide, and the antimony into the trioxide or sesquioxide, Sb_2O_3.

The oxide is then reduced with carbon:—

$$2\,Sb_2O_3 + 3\,C = 3\,CO_2 + 4\,Sb.$$

Compound of Antimony with Hydrogen — Stibine, SbH_3. — Antimony forms with hydrogen the compound SbH_3, which is analogous to the compounds of hydrogen with nitrogen, phosphorus, and arsenic.

NH_3	ammonia
PH_3	phosphine
AsH_3	arsine
SbH_3	stibine

COMPOUNDS OF ANTIMONY WITH OXYGEN AND HYDROGEN

With oxygen alone antimony forms three compounds: Antimony sesquioxide — Sb_2O_3, antimony tetroxide — Sb_2O_4, and antimony pentoxide — Sb_2O_5.

Acids of Antimony. — Antimony combines with hydrogen and oxygen, forming several compounds which are acids, but these are not so numerous as in the cases of phosphorus and arsenic. The best known of these is *antimonic acid*, having the composition H_3SbO_4. This is formed by the action of strong oxidizing agents such as nitric acid, or aqua regia, on antimony. It is also formed when the pentachloride of antimony is treated with water, which is analogous to the formation of phosphoric acid from phosphorus pentachloride: —

$$SbCl_5 + 4\,H_2O = 5\,HCl + H_3SbO_4.$$

Compounds of Antimony with Sulphur and the Metals. — We have seen that arsenic combines with sulphur and the metals, forming salts of sulpho-acids of arsenic. In an analogous

manner, antimony forms salts of sulpho-acids. When antimony trisulphide is treated with the sulphide of an alkali metal, such as potassium sulphide, ammonium sulphide, or polysulphide, the antimony trisulphide dissolves, forming a salt ($MSbS_2$) of meta-sulphantimonious acid ($HSbS_2$). The salt is a *meta-sulphantimonite*. Salts of *sulphantimonious* acid (H_3SbS_3) are also known.

When antimony pentasulphide is dissolved in an alkaline sulphide, salts of *sulphantimonic* acid are formed: —

$$Sb_2S_5 + 3\,Na_2S = 2\,Na_3SbS_4.$$

This compound, which contains nine molecules of water, is known as *Schlippe's salt.*

BISMUTH (At. Wt. = 208.3)

The last member of the nitrogen, phosphorus, arsenic, antimony family of group V in the Periodic System is bismuth. We have seen that as the atomic weight increases, the elements become less acidic, and the basic properties begin to manifest themselves. This condition, which has already appeared in antimony, is intensified in the element which we are now about to study, — bismuth.

Occurrence and Properties. — Bismuth occurs mainly in the free condition, but also combined with sulphur as the trisulphide, Bi_2S_3. Bismuth is obtained from the sulphide by burning out the sulphur with oxygen, when it is transformed into the oxide. The oxide is then reduced by carbon, yielding the element.

Some of the most important substances containing bismuth are certain of its alloys with other metals. These have the remarkable property that they fuse far below the melting-point of the lowest-melting constituent. The well-known *Rose's fusible metal* consists of one part of lead, one part of tin, and two parts of bismuth. It fuses at 93°.8.

There is an alloy of bismuth still more remarkable than the

above, in that it fuses at 60°.5. It is known as *Wood's metal.* This contains two parts of lead, one part of tin, four parts of bismuth, and one part of cadmium. It is the lowest-melting of these substances.

Compounds of Bismuth with Oxygen and Hydrogen. — While bismuth forms four compounds with oxygen, the only compound of importance is the sesquioxide, Bi_2O_3. It is formed when bismuth burns in the air. It combines readily with acids, forming water and the corresponding salt, and is, therefore, a base.

The corresponding hydroxide, $Bi(OH)_3$, also has decidedly basic properties.

Certain rare elements in this group of the Periodic System are: *vanadium, columbium, neodymium, praseodymium,* and *tantalum.*

EXPERIMENTS WITH PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

Experiment 100. Phosphorus an Active Element Chemically. — (Porcelain crucible; stone slab; filter-paper; carbon bisulphide; iodine; phosphorus.)

In a porcelain crucible resting on a stone slab under a hood introduce a piece of phosphorus dried by pressing between filter-paper. (*Never touch phosphorus with the hand, or severe burns may result.*) Allow the phosphorus to stand exposed to the air. White fumes will soon escape from the phosphorus, and its temperature may become high enough to cause it to ignite.

Finely divided phosphorus always takes fire in contact with the air. Dissolve a piece of phosphorus the size of a pea in 2 cc. of carbon bisulphide. Seize a piece of filter-paper with a pair of forceps and introduce it into the solution. Lay the filter-paper on a stone slab to dry. The carbon bisulphide quickly evaporates, leaving the phosphorus on the paper in a very finely divided condition. It always takes fire spontaneously under these conditions.

That *phosphorus combines with iodine by mere contact* can be seen by bringing into the porcelain crucible a piece of dry phosphorus the size of a pea, and throwing on to the phos-

phorus a few crystals of iodine. The two combine at once on contact. (See page 173.)

Experiment 101. Red Phosphorus more Stable than Yellow. —(Porcelain crucible; strip of metal 25 cm. long; iodine; red and yellow phosphorus.)

Bring a little iodine in contact with a little red phosphorus. They do not react. On the middle of a strip of metal, 25 cm. long, held at one end by a clamp, place side by side a piece of yellow and a piece of red phosphorus. Heat the other end of the strip. The yellow phosphorus will take fire first. Repeat the experiment, placing the red phosphorus 10 cm. from the end to be heated, and the yellow phosphorus 20 cm. from the end. Even under these conditions the yellow phosphorus will take fire first. (See page 173.)

Experiment 102. Compounds of Phosphorus and Hydrogen, Preparation. —(Glass flask holding 150 cc.; glass tubing; crystallizing-dish; sodium hydroxide; yellow phosphorus; hydrogen generator.)

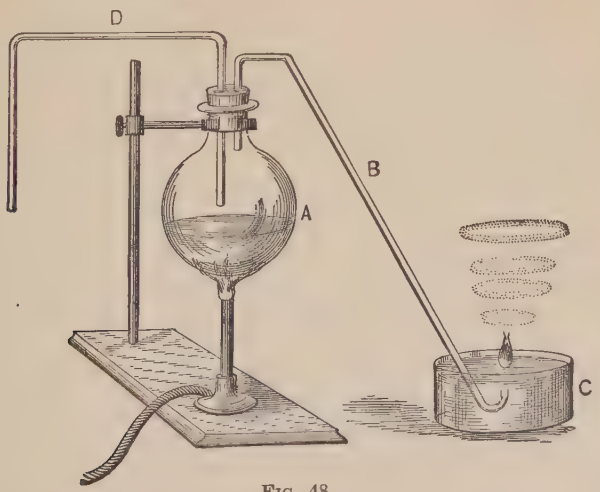

FIG. 48.

Set up the apparatus as in Figure 48 (under the hood). Ten grams of caustic potash are dissolved in 25 cc. of water, and the mixture cooled in ice-water. It is then introduced into the flask and two or three small fragments of phosphorus added. The flask is then closed tightly with the stopper. The tube

D is then attached to the hydrogen generator (a Kipp apparatus if convenient), and hydrogen is swept through the apparatus until all of the air has been removed. The rubber tube placed on the end of *D* is closed with a pinch-cock, and the hydrogen generator removed. The contents of the flask are then gently heated. The hydrogen is first driven out of the flask; then phosphine begins to escape, and as each bubble comes in contact with the air it takes fire spontaneously, producing a ring of white fumes which rises in the air. If the experiment is carried out in a place free from strong air-currents, the effect is very beautiful. The white fumes rise in a continuous ring, showing distinct vortex movement.

After the experiment is ended remove the flame and allow the water to flow back from the dish into the flask. Any gas remaining in the flask should be driven out by hydrogen before the flask is opened.

The inflammability is not due to the compound PH_3. If the gases escaping from the flask are washed by passing through a cylinder containing alcohol, they are no longer spontaneously inflammable on coming in contact with the air. The alcohol dissolves the compound P_2H_4, which is also formed in the above experiment, and which is the spontaneously inflammable constituent.

If in the above experiment considerable alcohol is added to the flask, this dissolves the compound P_2H_4 as fast as it is formed, and the escaping gas is no longer inflammable. (See page 174.)

Experiment 103. Phosphoric Acid formed when Water acts on Phosphorus Pentoxide. — (Phosphorus pentoxide; water.)

Add 100 cc. of distilled water to a beaker, and introduce, by means of a small porcelain spatula, quantities of phosphorus pentoxide not larger than a pea. Continue to add the pentoxide until a gram or so has dissolved in the water.

Filter a part of the solution; this contains chiefly metaphosphoric acid. Test the reaction of the solution towards litmus.

Boil the remainder of the solution, and the undissolved portion will pass into solution. This is a solution of orthophosphoric acid. Test its reaction with litmus. (See page 175.)

Experiment 104. Pyrophosphate formed by heating a Secondary Phosphate. — (Porcelain crucible; secondary sodium phosphate; porcelain crucible.)

Introduce a few grams of secondary sodium phosphate into a porcelain crucible, and heat gently over a bunsen burner until

all the water is removed. Then heat sharply over the blast-lamp. Dissolve the pyrophosphate in water and add a solution of silver nitrate. What do you observe? (See page 176.)

Experiment 105. Metaphosphate formed by heating Microcosmic Salt (Sodium Ammonium Acid Phosphate, $NaNH_4HPO_4$). — Heat a few grams of microcosmic salt in a porcelain crucible, first over a bunsen burner and then over a blast-lamp. Sodium metaphosphate results. (Equation?) Dissolve in water and add silver nitrate. What do you observe? (See page 176.)

Experiment 106. Arsenic sublimes without melting; burns on the Air; formed by reducing the Oxide with Carbon. — (Hard-glass tube, 15 cm. long, closed at one end; arsenic.)

Introduce one or two small pieces of arsenic into a hard-glass tube closed at one end, and heat this portion of the tube containing the arsenic. The arsenic will vaporize over the flame without melting, but will condense again on the colder walls of the tube.

Heat a small piece of arsenic on a piece of charcoal over the blast-lamp. White fumes of arsenic trioxide will be formed in abundance.

All of the experiments with arsenic must be carried out under a hood with a good draft. *The fumes of arsenic and its compounds are deadly poisonous if inhaled.*

Mix a little arsenic trioxide — white arsenic — with an equal volume of powdered charcoal, and introduce the mixture into a hard-glass tube closed at one end, through a funnel to prevent any of the mixture from adhering to the walls of the tube.

Heat the mixture; arsenic will be set free, and will distil out of this portion of the tube and condense on the colder walls of the tube. (See page 178.)

Experiment 107. Preparation of Arsine. — (Flask holding 500 cc.; safety-tube; calcium chloride tube; hard-glass tube drawn out as in Figure 48; pure zinc; dilute hydrochloric acid; white arsenic.)

The apparatus to be used is shown in Figure 49. The flask *A* contains pure zinc to which dilute hydrochloric acid is added. The hydrogen generated is passed through the tube filled with calcium chloride to dry it. After all the air has been driven out of the apparatus the hydrogen is ignited at *B*. It burns with a very nearly colorless flame, since the tube *B* is of hard glass. Introduce a piece of cold porcelain into the hydrogen flame; it will not be colored.

Now introduce into the flask *A*, through the safety-tube, a

few drops of a solution of arsenic trioxide in hydrochloric acid. The appearance of the flame of burning hydrogen will be changed at once. It will acquire a milky-white hue, and white fumes will escape. Introduce again the cold porcelain, and a

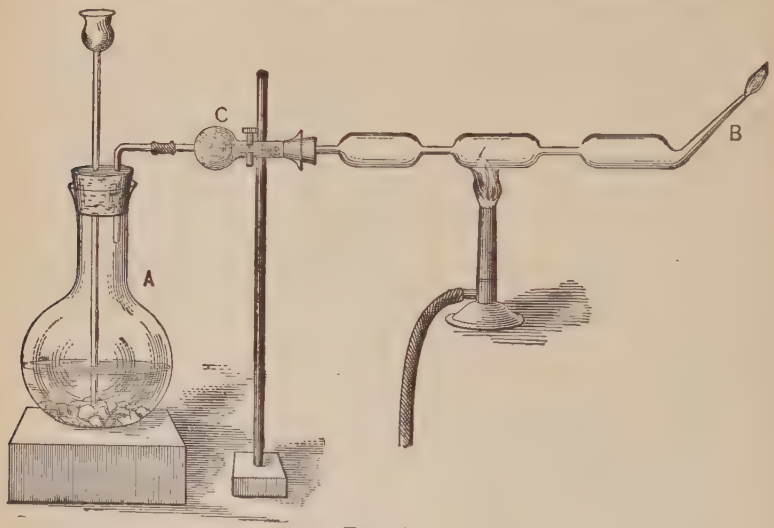

FIG. 49.

dark spot will be deposited upon it. This is the so-called *arsenic mirror*. Observe carefully its metallic appearance. Pour over the arsenic mirror a solution of sodium hypochlorite. The arsenic will be dissolved. (See page 178.)

Experiment 108. Arsine decomposed by Heat. — Heat one of the expansions in the glass tube (Fig. 48). The arsine will be decomposed, and a mirror of arsenic will be deposited upon the glass just beyond the flame. Interrupt the experiment, open the glass tube, and add a solution of sodium hypochlorite and shake. Does the arsenic dissolve? (See page 178.)

Experiment 109. Arsenic Trisulphide. — (Test-tube; hydrogen sulphide generator; white arsenic; hydrochloric acid; yellow ammonium sulphide.)

Dissolve a little white arsenic in hydrochloric acid and pass a stream of hydrogen sulphide through the solution. Yellow arsenious sulphide is precipitated. Write the equation?

Filter off the solid sulphide and wash with hot water. To the

solid sulphide on the filter-paper add yellow ammonium sulphide. The arsenic sulphide passes into solution, forming the sulpho salt. Write the equation? (See page 179.)

Experiment 110. Fusion of Antimony; Combustion of Antimony in Contact with the Air. — (Antimony; piece of charcoal; blowpipe.)

When a piece of antimony is heated on charcoal by means of a mouth-blowpipe it melts. When the molten globule is thrown on a piece of white paper, it runs over the surface of the paper, and often produces beautiful, fantastic designs. If the piece of charcoal on which the antimony was melted be examined, it will be found to contain a white coating which is an oxide of antimony. Compare this with the coating produced by arsenic? It is less volatile than the oxide of arsenic, and remains on the charcoal closer to the flame of the blowpipe. (See page 180.)

Experiment 111. Preparation and Properties of Stibine. — (Same materials as in Experiment 107; instead of arsenic trioxide use a solution of tartar emetic or of antimonious chloride, to which some tartaric acid has been added.)

Arrange the apparatus exactly as in Figure 48, and prepare stibine exactly as arsine was prepared. Burn the mixture of hydrogen and stibine and note the color of the flame. Introduce a cold piece of porcelain, and a dark spot will be deposited — the *antimony mirror*. The spot of antimony is dull in appearance, and thus differs from the bright lustrous spot of arsenic. The antimony mirror is insoluble in sodium hypochlorite, and this distinguishes it unquestionably from arsenic.

When the tube through which the stibine is passing is heated, the stibine is decomposed and antimony is deposited on the walls of the tube. The antimony being less volatile than the arsenic is deposited nearer the flame. (See page 180.)

Experiment 112. Antimony Sulphide. — (Solution of tartar emetic; hydrogen sulphide generator.)

Pass hydrogen sulphide into a solution of tartar emetic to which a few drops of hydrochloric acid have been added. Brick-red antimony sulphide is precipitated. Filter the solid from the solution and wash the precipitate on the filter-paper. Add to the filter-paper containing the antimony sulphide some yellow sulphide of ammonium. The sulphide of antimony will dissolve. What is formed? Write equation? (See page 181.)

Experiment 113. Oxidation of Bismuth on the Air. — (Piece of charcoal; blowpipe; bismuth.)

Heat a piece of bismuth on charcoal with the blowpipe. What is the color of the oxide formed on the charcoal? Is it very volatile? Compare with the results obtained with arsenic and antimony.

Experiment 114. Bismuth Sulphide. — (Bismuth nitrate; nitric acid; hydrogen sulphide generator.)

Dissolve bismuth nitrate in water containing nitric acid and pass hydrogen sulphide into the solution. Black bismuth sulphide is precipitated. Filter off; test solubility in dilute hydrochloric and nitric acids? In concentrated hydrochloric and nitric acids?

PROBLEMS

1. How much phosphorus could be obtained from a kilogram of bone-ash, if bone-ash were pure tricalcium phosphate? Amount of phosphine obtainable from the above amount of phosphorus?
2. How much phosphoric acid can be obtained from 5 kilograms of bone-ash, assuming that bone-ash is pure tricalcium phosphate?
3. Weight of hydrogen ions obtainable from 10 grams of orthophosphoric acid, if the dissociation of each molecule into three hydrogen ions was complete?
4. When 3.7 grams of secondary sodium phosphate is heated, how much pyrophosphate would be formed? How much metaphosphate would be formed from the same weight of primary sodium phosphate?
5. Weight of arsenic trioxide that can yield 7.9 grams of arsine?
6. Weight of stibine obtainable from the antimony in 3.1 grams of stibnite?
7. The bismuth in 5 grams of the compound Bi_2S_3 will form what weight of the hydroxide $Bi(OH)_3$?

CHAPTER XVII

CARBON, SILICON, BORON

CARBON (At. Wt. = 12.0)

We now come to one of the most important elements in the whole field of chemistry. This is the first member of group IV — Carbon. This element is important as being an essential constituent of every living thing, from the simplest organism to the most complex.

Allotropic Forms of Carbon: Diamond and Graphite. — We know carbon in several modifications, both crystallized and amorphous. There are two crystalline modifications, known respectively as *diamond* and *graphite*. The *diamond* is carbon and nothing but carbon, as is shown by the fact that when the diamond is burned in oxygen, it is converted completely into a compound of carbon; and when this compound is collected and weighed, the amount of carbon present in the compound is exactly equal to the weight of the original diamond.

Diamonds have now been made artificially — a problem which has attracted great attention in time past. The French chemist Moissan was the first to solve this problem as far as small diamonds are concerned. In 1893 he prepared diamonds in connection with his beautiful investigations at very high temperatures obtained by means of the *electric furnace*. The largest diamond which Moissan has thus far prepared has a diameter of only 0.5 mm.

The preparation of large diamonds artificially is as yet an unsolved problem.

Another crystalline modification of carbon is known as *graphite* or *plumbago*. While the diamond is comparatively rare, graphite occurs in nature in considerable quantities, especially

in Siberia. Graphite can readily be prepared by heating amorphous carbon, such as ordinary charcoal, in an electric furnace, or better, by dissolving carbon in molten metals and allowing it to crystallize.

Amorphous Forms of Carbon. — Carbon occurs in the uncrystallized condition in many forms. One of the best known is *charcoal*, or *wood charcoal* as it is usually termed. If a piece of wood is heated to a high temperature in the presence of an abundance of oxygen, the carbon unites with the oxygen, forming the well-known compound, carbon dioxide. If, on the other hand, wood is heated without free access of air, many products are formed, but the carbon remains behind for the most part as charcoal.

Bone-black is another form of amorphous carbon obtained by the destructive distillation of bones. To obtain it in pure form the inorganic matter contained in the bones is dissolved out by some strong acid.

Soot or *lamp-black* is an amorphous form of carbon obtained by introducing a cold object into the flame of an ordinary lamp. Under these conditions some of the carbon, before it combines with oxygen, is deposited in a very finely divided condition known as lamp-black or soot.

Coal or *stone-coal* is the form in which free carbon occurs most abundantly in nature. There are great beds of these deposits in many places on the earth, and these are of fundamental importance for the welfare of the human race. In coal we find vast quantities of intrinsic energy which can readily be converted into other forms, and our steam engines, electric motors, electric light plants, etc., are all dependent upon coal for their utility.

These deposits of coal are chiefly of vegetable origin. In certain localities, where there has been a great accumulation of vegetable matter, this has undergone decomposition without free access of air and the carbon has been deposited in the form of coal.

If the coal is hard and comparatively free from volatile oils,

it is called *anthracite;* if it is soft and contains much volatile matter, it is known as *bituminous* coal. If the process of coal formation is not very far advanced, we have *peat, lignite,* etc.

The Different Forms of Carbon contain Different Amounts of Energy. — It is obvious from the above that many forms of carbon are known. The question arises, How do these forms differ from one another? They are all carbon, and materially considered nothing but carbon, and yet have very different properties. We have met with analogous cases in the different modifications of oxygen, sulphur, and phosphorus, and found in every one of these cases that the different modifications of the same element contain different amounts of intrinsic energy. We would naturally look for the same differences in the case of carbon.

The heats of combustion of different modifications of carbon were determined and the following results obtained: —

	Heat of Combustion
Charcoal	96.980 calories
Retort carbon	96.530 calories
Diamond	94.550 calories
Graphite	93.360 calories

Since the end product is the same in every case, — carbon dioxide, — the differences between the heats of combustion of the various forms of carbon are a measure of the different amounts of intrinsic energy in these different forms.

We see that these differences are quite considerable, amorphous carbon having the largest amount of intrinsic energy and the crystallized varieties the least.

Physical Properties of Carbon. — Carbon, except in the form of the diamond, is a black solid, hard, and having a more or

less metallic lustre in graphite and anthracite, soft in wood charcoal and coke, and a fine powder in soot or lamp-black.

Carbon remains solid until an enormously high temperature is reached. In the electric arc, where the temperature is probably in the neighborhood of 3500°, carbon vaporizes, but even at this enormously high temperature, comparatively slowly.

COMPOUNDS OF CARBON

Compounds of carbon with hydrogen, oxygen, nitrogen, sulphur, etc., are known in such large numbers that a separate branch of chemistry has grown up around the element carbon.

While the study of the compounds of carbon belongs to organic chemistry, we shall take up a few typical, fundamental substances, to give an idea of the kind of compounds which carbon forms with other elements.

Compounds of Carbon with Hydrogen. — Carbon forms with hydrogen a very large number of compounds. Indeed, these two elements form several series of compounds; the individual members of any series differing in composition by one carbon atom and two hydrogen atoms. The simplest compound of carbon and hydrogen has the composition CH_4, and is known as marsh gas, or *methane*.

There is a series of compounds closely related to methane, and known as the methane series. The simpler members are —

Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}

Carbon forms with hydrogen a compound containing just twice as much carbon in proportion to hydrogen as methane. This compound has the composition C_2H_4, and is known as *ethylene*. This, like methane, is a fundamental substance, and the first member of a group of hydrocarbons which have a constant difference in composition.

The first few members of this group are: —

Ethylene	C_2H_4
Propylene	C_3H_6
Butylene	C_4H_8

Such series of compounds as the above, in which successive members differ in composition by the group CH_2, are known as *homologous* series of compounds.

The above series, of which several members are known, is the ethylene series of hydrocarbons.

Carbon forms other series of compounds with hydrogen, but it would lead us too far to discuss them in this connection. The *acetylene* hydrocarbons, the first member of which is acetylene, C_2H_2, should, however, be mentioned.

Compounds of Carbon with Oxygen. — Carbon forms two compounds with oxygen, — carbon monoxide, CO, and carbon dioxide, CO_2.

Carbon Monoxide, CO. — Carbon monoxide is formed by the direct union of the two elements. When carbon is heated in a limited supply of oxygen, the product is carbon monoxide.

The most convenient method of preparing carbon monoxide is by heating formic acid, a compound having the composition H_2CO_2, with concentrated sulphuric acid. This decomposes as follows: —

$$H_2CO_2 = H_2O + CO.$$

Carbon monoxide is a colorless, poisonous gas. When breathed into the system it combines with the hæmoglobin of the blood and prevents the latter from carrying out its normal function, which is to carry oxygen to the various organs of the body.

Carbon monoxide is frequently formed in the incomplete combustion of carbon in poorly ventilated furnaces. From such furnaces it easily escapes into the room, and is breathed by the inhabitants. If the room into which carbon monoxide is escaping is poorly ventilated, bad results may follow.

o

Carbon monoxide combines directly with oxygen, forming carbon dioxide, and is, therefore, a good reducing agent. When carbon monoxide is brought in contact with the hot oxides of the heavy metals, they are reduced to the metallic condition, and the carbon monoxide is oxidized to carbon dioxide.

Thermochemistry of Carbon Monoxide. — When a gram-atomic weight (12 grams) of carbon is burned to carbon monoxide, the amount of heat set free is only about 20,000 calories, while about 70,000 calories are liberated when carbon monoxide is oxidized to carbon dioxide. Carbon monoxide, therefore, contains a large amount of intrinsic energy which can be converted into heat by simply oxidizing it to carbon dioxide. It is due to this fact that carbon monoxide is an excellent heating agent.

Water-gas. — One of the methods for preparing carbon monoxide is to pass water-vapor over highly heated carbon; the action which takes place being —

$$C + H_2O = CO + H_2.$$

This mixture of carbon monoxide and hydrogen would have very little value as an illuminating gas, since both of these gases burn with a comparatively colorless flame, although they evolve an enormous amount of heat. This mixture of gases is passed through highly heated petroleum vapor, and is thus mixed with hydrocarbons and other substances which give off an abundance of light when they are burned. This mixture, known as *water-gas*, is now used largely for illuminating purposes.

Water-gas is now extensively used where illuminating gas, made by the dry distillation of coal, was formerly employed.

Carbon Dioxide, CO_2. — The highest product of the direct oxidation of carbon is carbon dioxide. This compound occurs in a number of places in the free condition. It is one of the constituents, as will be remembered, of atmospheric air. It also occurs dissolved, in greater or less quantity, in water.

Carbon dioxide escapes from certain mineral springs dissolved in the water of such springs.

When the water reaches the surface of the earth, a part of the gas escapes and gives the characteristic effervescence.

Carbon dioxide is given off by animals, as can be readily shown by breathing for a short time into lime-water or a solution of barium hydroxide, when insoluble calcium or barium carbonate is formed.

Carbon dioxide is also set free when animal and vegetable matter decomposes, and also in many processes of fermentation.

Preparation of Carbon Dioxide. — Carbon dioxide can be prepared by a number of methods. Theoretically, one of the simplest methods is to burn carbon in an excess of air: —

$$C + O_2 = CO_2.$$

Practically, a far more convenient method of preparing carbon dioxide is to treat a carbonate with an acid: —

$$K_2CO_3 + 2\ HCl = 2\ KCl + H_2CO_3.$$

The hypothetical compound H_2CO_3 breaks down thus: —

$$H_2CO_3 = H_2O + CO_2.$$

When certain compounds are heated, they readily lose carbon dioxide, while others lose it only at high temperatures. The carbonate of calcium, or ordinary limestone or marble, belongs to the former class. When this substance is heated, it breaks down thus: —

$$CaCO_3 = CaO + CO_2.$$

Chemical Properties of Carbon Dioxide. — The most characteristic chemical property of carbon dioxide is its power to form salts in the presence of aqueous solutions of alkalies. When one equivalent of caustic potash, in water, is brought into the presence of one equivalent of carbon dioxide, the following reaction takes place: —

$$KOH + CO_2 = KHCO_3.$$

When two equivalents of caustic potash are used, we have the following reaction: —

$$2\ KOH + CO_2 = K_2CO_3 + H_2O.$$

The first salt is acid potassium carbonate, the second normal potassium carbonate.

Carbon dioxide in the presence of water acts, then, as a dibasic acid.

The aqueous solution reacts slightly acid, showing that there are a small number of hydrogen ions present: —

$$H_2CO_3 = \overset{+}{H},\ H\overset{-}{C}O_3.$$

The acid is so weak that we are not justified in assuming that there is any dissociation of the ion, $H\overset{-}{C}O_3$, in the presence of water alone. When an alkali is present, and all the hydrogen ions from the first stage of dissociation are used up, it is probable that the ion, $H\overset{-}{C}O_3$, begins to dissociate thus: —

$$H\overset{-}{C}O_3 = \overset{+}{H} + \overset{=}{C}O_3,$$

and this dissociation continues to the end if there are enough hydroxyl ions from the base present to combine with all the hydrogen ions as rapidly as they are formed.

The carbonates, like the salts of all weak acids, are *hydrolyzed* (see page 176) *by water*. This is shown by the fact that a salt like sodium carbonate shows a strongly alkaline reaction, which means that there are hydroxyl ions present: —

$$Na_2CO_3 + H_2O = \overset{+}{N}a,\ O\overset{-}{H} + \overset{+}{N}a,\ H\overset{-}{C}O_3.$$

The hydrolysis of carbonates is by no means complete, only a comparatively small number of molecules being broken down by the water as represented in the above equation.

REDUCTION OF CARBON DIOXIDE BY PLANTS

Carbon dioxide is being continually reduced by green plants in the sunlight. They build up the carbon into complex com-

pounds with hydrogen, oxygen, and perhaps nitrogen, and these compounds contain enormous amounts of intrinsic energy. The complex compounds of carbon are consumed by animals, which decompose these substances into much simpler ones, especially into carbon dioxide. The large excess of intrinsic energy in the complex compounds over that in the simpler products which animals excrete, is converted into heat and by the animal into mechanical work.

The chief source of the energy which animals expend is, then, the complex compounds of carbon, which are built up by plants from carbon dioxide.

It is of interest to note that most of the carbon in animal and vegetable tissues ultimately passes off when these decay, in the form of carbon dioxide. The carbon dioxide is again taken up by the plant, converted into complex compounds, consumed by the animal, broken down into simpler substances, and the cycle is thus completed.

Physical Properties of Carbon Dioxide. — The gas carbon dioxide can be readily liquefied. Carbon dioxide is liquefied on a large scale by pumping it into thick-walled, steel cylinders, which are kept cool. Such cylinders are kept in the laboratory as sources of supply of carbon dioxide.

When the carbon dioxide is allowed to escape from such cylinders through a fine opening, part of it volatilizes and escapes as a gas, while the remainder is converted into the solid condition and can be caught in a bag placed over the jet. Solid carbon dioxide is a compact white mass resembling compressed snow. It has been extensively used as a refrigerating agent.

Compounds of Carbon with Oxygen and Hydrogen. — Thousands of such compounds are known. While these belong strictly to the subject of organic chemistry, a few typical substances will be considered here.

The *alcohols* are among the simplest of the compounds of carbon with oxygen and hydrogen. The first member of this series of compounds is methyl alcohol, CH_4O, or wood spirit,

as it is termed. The alcohols form a homologous series of compounds which are analogous to the hydrocarbons. The first members of this series are: —

Methyl alcohol	CH_4O
Ethyl alcohol	C_2H_6O
Propyl alcohol	C_3H_8O

A product of the oxidation of an alcohol is an *ether*. Take ordinary ethyl ether. This has the composition $C_4H_{10}O$, and is a member of a homologous series of compounds. The first member is methyl ether, C_2H_6O, the second methyl-ethyl ether C_3H_8O, and so on.

If an alcohol is further oxidized, it passes over into an *acid*, and we have homologous series of organic acids. If ethyl alcohol is properly oxidized, we have acetic acid, CH_3COOH. This is the second member of the formic acid series, formic acid being the first.

Formic acid	$HCOOH$
Acetic acid	CH_3COOH
Propionic acid	C_2H_5COOH

Compound of Carbon with Sulphur, CS_2. — Carbon bisulphide, CS_2, is formed by passing the vapors of sulphur over highly heated carbon. The two elements unite, forming carbon bisulphide, which, being volatile, passes out of the field of action. Carbon bisulphide is very easily inflammable, readily uniting with oxygen and forming carbon dioxide and sulphur dioxide.

Carbon bisulphide is an excellent solvent, not only for oils, fats, and other complex organic compounds, but for bromine and iodine and many other substances. It is a liquid with a highly disagreeable odor, boiling at 46°.

Compound of Carbon with Nitrogen — Cyanogen $(CN)_2$. — When we consider the inert nature of the element nitrogen, it is surprising that the compound $(CN)_2$ should be capable of existence. The two elements, however, do not combine directly, but combine readily with an alkali metal, forming

such compounds as potassium cyanide, KCN. Cyanogen is not so readily obtained from the potassium compound, but is very easily prepared from mercuric cyanide. This compound when heated breaks down into mercury and cyanogen: —

$$Hg(CN)_2 = Hg + (CN)_2.$$

Cyanogen is a gas which is characterized by *its extremely poisonous nature.*

Hydrocyanic Acid, HCN. — Hydrocyanic acid is formed when a cyanide is treated with an acid: —

$$MCN + HCl = MCl + HCN.$$

This acid, which is very soluble in water, is known as *prussic acid.* It is characterized by *its extremely poisonous nature.* Hydrocyanic acid is a very weak acid. It dissociates into $\overset{+}{H}$, $\overset{-}{CN}$, but only to a slight extent. When there is a strong alkali present, which is the same as to say an excess of hydroxyl ions, the hydrogen ions are used up as fast as they are formed, combining with the hydroxyl ions to form water, and more of the acid dissociates.

THE RÔLE OF CARBON IN PRODUCING LIGHT

Illumination. — The subject of the production of light or illumination is one that has attracted attention for a very long time. In practically all of the earlier methods of producing light, and in many of those used to-day, carbon is employed in one form or another. Most of the methods of illumination owe their existence to some compound of carbon which is burned or oxidized, giving out heat and light.

Candle and Oil-lamp. — In the candle we have complex compounds of carbon which at ordinary temperatures are solid. These are made by melting the stearine, tallow, or paraffine, and pouring the liquid into a mould after a wick has been placed in the centre of the mould. The object of the wick is

to carry by capillarity the material of the candle, as it is melted, up into the flame. The tip of the candle is melted, and the end of the wick ignited. This melts a portion of the solid hydrocarbons, which are carried up by the wick into the flame and are burned, the heat set free melting more of the solid, and the process is thus a continuous one. The heat and light are derived from the breaking down of complex compounds of carbon into simpler substances, and the oxidation of the carbon to carbon dioxide.

In our oil-lamps the compounds of carbon which are to be burned are liquid at ordinary temperatures. These are carried up into the flame by means of the wick, as in the candle, and the same general processes are involved in the production of light and heat.

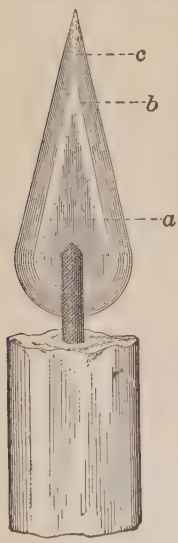

FIG. 50.

Flames and their Luminosity.—If we examine a typical flame, say that of a candle, we observe three distinct parts: An inner cone *a* (Fig. 50), of unburned gases, is surrounded by a zone *b*, of partially oxidized substances. It is in this zone that acetylene, which has much to do with the light-giving power of the flame, is formed. This zone is the chief source of light in the flame. This is surrounded by a third layer *c*, of burning gases, and here, where there is an abundant supply of oxygen from the air, the processes of oxidation are completed. This part of the flame is relatively only slightly luminous.

So much for the structure of a flame. The question remains, What are the causes of the luminosity of flames? We have seen that the chief source of light in a flame is in the middle zone, where the combustion is not complete. This gave rise to the theory that the chief source of light in a flame is unburned, solid particles of carbon, which become heated to incandescence. These particles come from the compounds of carbon which are decomposed by the heat of

the flame. This theory accounts for many of the facts concerning the luminosity of flames, but by no means for all.

Hydrogen gas at atmospheric pressure burns with an almost non-luminous flame. Hydrogen gas, under high pressure, however, burns with a luminous flame. The *effect of pressure on luminosity* is also shown by burning a candle in a valley and on a high mountain. Under the former conditions, where the pressure is relatively high, the luminosity is much greater. Further, gases which burn with a luminous flame can be made to burn with a relatively non-luminous flame by *mixing them with an indifferent gas, or by simply cooling them.*

These facts cannot by any means be all explained on the solid particle theory of luminosity. There are undoubtedly many influences which affect the luminosity of flames, so that probably no one theory can account for all of the facts connected with this phenomenon.

According to recent investigations it seems very probable that the formation and oxidation of acetylene in flames is vitally connected with their light-giving power.

Bunsen Burner; Blowpipe. — Practical use is made of the fact that complete oxidation, and also the dilution of a gas with an indifferent gas, lowers its luminosity, in constructing the *bunsen burner.*

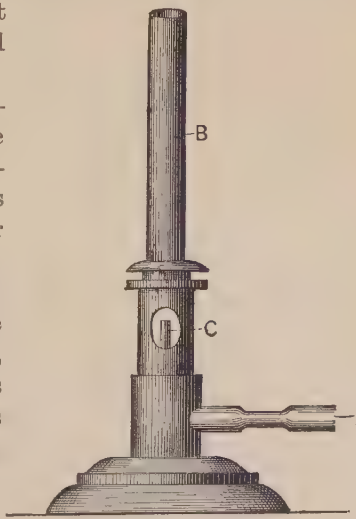

FIG. 51.

A bunsen burner is shown in Figure 51. The gas enters through the horizontal tube *A*, into the vertical tube *B*. Air enters through the hole *C*, and mixes with the gas. The flame consists of two distinct parts: an inner blue cone, where the oxidation is far from complete, and which is known as the

reducing flame, since it has remarkable power to combine with oxygen and reduce substances such as the oxides of the metals; and an outer, almost non-luminous tip, where the oxidation of the gas is completed and where the temperature is very high. This is known as the *oxidizing flame,* on account of its power to give up oxygen to substances which can be oxidized. Metals, for example, in this flame are usually converted into oxides.

By means of the bunsen burner very high temperatures can be secured by the combustion of illuminating gas, without the production of any appreciable quantity of light.

When a cold object is inserted into the flame of a bunsen burner, no carbon is deposited upon it in the form of soot, and the lamp is, therefore, very convenient for heating where cleanliness is absolutely essential. The bunsen burner is one of the most frequently used pieces of apparatus in the chemical laboratory.

The blowpipe is a still more efficient means of obtaining a clean oxidizing and a clean reducing flame, and of directing these flames where they are desired. The blowpipe itself is shown in Figure 52. It consists of a tube t, into which the breath is blown from the mouth, and a tube t_1, at right angles to this, through which the air from the lungs passes into the flame. Into the top of an ordinary bunsen burner is inserted a tube with a narrow opening, so as to give a narrow flame.

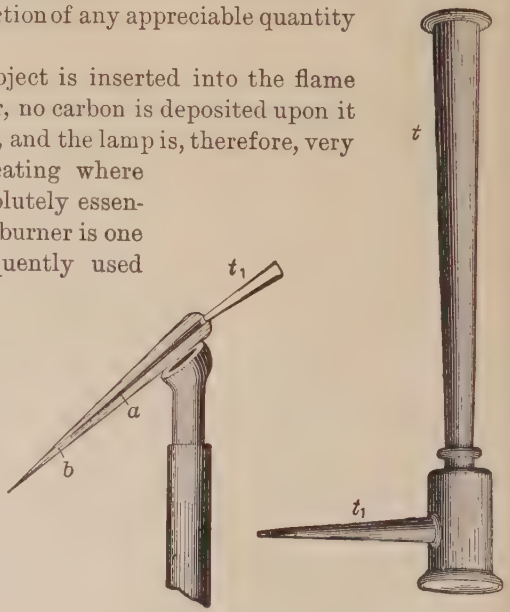

FIG. 52.

The blowpipe is placed upon the upper edge of this tube, as indicated in the drawing, and the breath expelled continuously through the tube. The combustion of the gases is excellent, and the flame takes the form shown in the figure. The inner flame *a* is the reducing flame, and the outer tip *b* the oxidizing portion of the flame.

By means of the blowpipe flame very delicate work can be done. In the reducing flame small quantities of metal oxides can be reduced to the metallic condition, and identified.

Effect of Cooling the Flame. — The effect of cooling the flame can be readily shown by means of the following experiment: Open an ordinary gas stop-cock, and a short distance above the orifice hold a wire gauze with fine mesh. Light the gas above the gauze, and it will burn without the gas below the gauze taking fire. This is due to the fact that the metallic gauze conducts the heat away so rapidly, that the gas below the gauze is not heated to its *kindling temperature* and does not ignite.

This principle was made use of by Sir Humphry Davy in the construction of his *safety lamp* for use in mines where explosive gases are liable to accumulate. The flame is simply surrounded by a fine wire gauze. If the explosive gases should ignite on the inside of the gauze, the flame cannot propagate itself through the gauze, since it is too greatly cooled. The gauze, conducting the heat from the flame, prevents the gases on the outside from becoming heated to their kindling temperature, and thus explosions are avoided when lights are carried into an atmosphere containing explosive gases.

The Welsbach Light. — The Welsbach light differs from the ordinary gas-light in that solid substances are introduced into the flame, which, when hot, have remarkable light-giving power. The Welsbach light depends for its value entirely upon the *mantle*. The mantle consists of a mixture of thorium and cerium oxides. It is prepared as follows: Fine cotton thread is woven into exactly the form of the mantle. This is saturated with an aqueous solution of a mixture of the nitrates of thorium and cerium. This mixture contains 99 per cent of the

thorium salt and one per cent of the cerium salt. The mantle is then dried and highly heated to burn out all organic matter, and to convert the cerium and thorium nitrates into the oxides. It is then ready for use.

It is a remarkable fact that if the amount of cerium salt added to the thorium is either increased or diminished appreciably, the light-giving power of the Welsbach burner is greatly diminished.

The value of the burner is to be found in the power of these oxides to convert heat energy in large quantity into light energy, so that the final result is a conversion of more of the intrinsic energy of the carbon compounds and other substances in the gas into light energy.

The Electric Light. — At first sight the relation between carbon and the electric light may not appear to be very close, other than the use of carbon as the source of energy to drive the dynamo which generates the electrical energy.

To obtain light energy from electrical energy, a resistance to the passage of the electrical current is interposed. The current is usually passed between two carbon poles, which are heated to such a high temperature that the carbon is partially volatilized. At this temperature the highly heated carbon gives off an enormous amount of light energy, and this is the source of the light in the electric arc-light. In the incandescent light the carbon is heated white-hot in a vacuum or an inert gas, and gives out light without undergoing any appreciable chemical change.

SILICON (At. Wt. = 28.4)

The second member of the fourth group in the Periodic System is silicon. This element is very widely distributed over the surface of the earth, and constitutes an important part of most rocks. Silicon occurs in great abundance as the dioxide, and forms an acid — silicic acid, whose salts make up many of our best-known rocks. Silicon dioxide, or *quartz*, also occurs in huge masses, and is a constituent of many rocks, especially

granites, gneisses, etc. Silicon dioxide occurs in great abundance as *sand,* especially along the edges of large bodies of water.

Preparation of Silicon. — Silicon is prepared from its compounds by a number of methods. One of these consists in heating silicon tetrafluoride with sodium: —

$$SiF_4 + 4\,Na = 4\,NaF + Si.$$

Silicon Hydride or Hydrogen Silicide, SiH_4. — Silicon forms a compound with hydrogen, known as silicon hydride, or hydrogen silicide, containing one atom of silicon united with four atoms of hydrogen. It also forms the compound Si_2H_6, which is spontaneously inflammable.

As far as composition is concerned, silicon tetrahydride is analogous to methane, — SiH_4, — CH_4. The former, however, is very unstable, while the latter is quite stable.

Silicon Dioxide, SiO_2. — Silicon forms one compound with oxygen, — silicon dioxide. This is analogous to carbon dioxide. It does not form the analogue of carbon monoxide.

Silicon dioxide occurs in nature in great abundance. It is beautifully crystalline in several varieties of *quartz,* such as *amethyst, rock crystal,* and the like, and, with certain impurities which give it color, it is of more or less value as gems, such as *opal, jasper, onyx, agate,* etc.

It occurs in great masses in less attractive forms, such as *quartz, sand, flint, sandstone,* and the like, and is frequently the chief constituent of large mountain ranges. When we consider the abundance of the two forms, quartz and sandstone, we can see the importance of the element silicon in the inorganic world, and from a geological standpoint.

Silicon dioxide is very resistant to chemical reagents, and is not attacked by acids, with the exception of hydrofluoric. When powdered very finely and fused with a caustic alkali, or an alkaline carbonate, it is transformed into a silicate: —

$$SiO_2 + 2\,KOH = K_2SiO_3 + H_2O.$$

This is a salt of a silicic acid having the composition H_2SiO_3.

The Acids of Silicon. — Silicon combines with hydrogen and oxygen, forming a number of acids which, however, can all be regarded as derived from one mother-substance, — normal silicic acid. When an alkaline silicate like that mentioned above is treated with an acid, the following reaction probably takes place: —

$$K_2SiO_3 + 2\,HCl + H_2O = 2\,KCl + H_4SiO_4.$$

The compound H_4SiO_4 is known as *normal silicic* acid, or *orthosilicic* acid.

When the normal acid is heated, it loses water and forms silicon dioxide: —

$$H_4SiO_4 = 2\,H_2O + SiO_2.$$

Polysilicic acids can all be regarded as derived from the acid H_4SiO_4, by removal of one or more molecules of water from two or more molecules of the acid. Thus, by the removal of one molecule of water from two molecules of normal silicic acid, we have: —

$$2\,H_4SiO_4 = H_2O + H_6Si_2O_7.$$

By removing two molecules of water: —

$$2\,H_4SiO_4 = 2\,H_2O + H_4Si_2O_6.$$

This series of acids, salts of some of which are known, suggest the homologous compounds of carbon. The constant difference with carbon is the group CH_2. The constant difference with silicon is the molecule of water H_2O.

Some of the salts of the polysilicic acids are very important substances, since they constitute many of the most abundant silicates.

Conversion of Silicates into Carbonates. — Notwithstanding the great stability and insolubility of the silicates, they are being decomposed all over the surface of the earth by such a weak acid as carbonic acid. This *carbonation* is taking place all over the surface of the earth, wherever the carbon dioxide in the air and in the waters comes in contact with silicates. This, at first sight, is very surprising. How is it possible for

such a weak acid as carbonic acid to displace silicic acid from the very stable silicates? This is especially difficult to understand when we consider that carbonic acid is so easily volatile, and therefore escapes from the field of chemical action.

The explanation is to be found in *the effect of mass on chemical activity*. This is one of the very best examples of mass action, as conditioning the *direction* as well as the *magnitude* of chemical action.

The great amount of carbon dioxide in the air and in the water, acting slowly but continually for a long period of time, effects a reaction which, in the laboratory, would be impossible.

The above process is of great geological and economical importance. By this means in part, many of the most resistant rocks are decomposed and the surface of the earth greatly changed in appearance. This process is of importance in that the constituents of rocks are made available for plants.

Compound of Silicon with Fluorine — Silicon Tetrafluoride, SiF_4. — The compound of silicon and fluorine, SiF_4, is of special interest, since it is the compound formed when hydrofluoric acid acts on glass. Silicon tetrafluoride is formed by the action of hydrofluoric acid on silicon dioxide. Since hydrofluoric acid is prepared most conveniently by the action of sulphuric acid on calcium fluoride, silicon tetrafluoride is prepared by mixing sand, calcium fluoride, and sulphuric acid.

Carborundum, SiC. — A compound of silicon with carbon should be mentioned on account of its remarkable composition and properties. This is the compound SiC, known as carborundum. It is formed by heating in an electric furnace a mixture of carbon and finely powdered sand. Carborundum is remarkably hard, and is technically useful on account of this property. It is very resistant to chemical reagents.

In this same group the rare elements, *germanium*, *titanium*, *zirconium*, *cerium*, and *thorium* occur.

BORON (At. Wt. = 11.0)

We pass now to group III of the Periodic System, the first

member of which is boron. This is the only member of this group which has distinctly acid-forming properties. We shall, therefore, take up boron in the present connection, and the remaining members of the group considerably later, when we come to study the base-forming, or metallic elements.

Occurrence, Preparation, and Properties. — The borates, or salts of boric acid, are the chief source of the element boron. Boron is prepared by the reduction of the trioxide of boron. In preparing boron the nitrogen of the air must be excluded by a layer of borax, since nitrogen combines with boron at high temperatures. Boron forms beautiful crystals, which are characterized by their great hardness. They seem to have nearly the same hardness as the diamond. *Boron trioxide* is formed by burning boron in oxygen: —

$$4\,B + 3\,O_2 = 2\,B_2O_3.$$

Boron trioxide is the anhydride of boric acid, which we shall now study.

Boric Acid, H_3BO_3. — Boric acid occurs in nature in the free condition. It is volatile with water-vapor, and in the region of certain hot springs, as in Tuscany, it is brought to the surface of the earth by the escaping vapors.

Boric acid is soluble in water, forming beautiful white crystals when the aqueous solution is evaporated. It is easily recognized by the fact that its alcoholic solution burns with a characteristic green flame. If boric acid, or a borate treated with sulphuric acid, is treated with a little alcohol and the alcohol ignited, the flame appears green throughout if there is much boric acid present. If only a small amount of boric acid is present, the flame is green only on the edges.

The salts of the normal boric acid, H_3BO_3, do not exist.

Boric acid can lose water and form an acid whose salts are well known: —

$$4\,H_3BO_3 = 5\,H_2O + H_2B_4O_7.$$

The acid $H_2B_4O_7$ is known as *tetraboric acid*, and its sodium salt, $Na_2B_4O_7$, $10\,H_2O$, is ordinary *borax*. Borax melts easily,

forming a colorless liquid. This liquid has the power of dissolving certain metal oxides and forming with them, when cold, glass-like masses which have characteristic colors. The *borax bead* is, consequently, of importance in blowpipe analysis for the detection of metals.

Boron Nitride, BN, is formed by the direct union of nitrogen with boron at an elevated temperature.

Summary. — We have studied thus far oxygen, hydrogen, and the halogens or members of group VII in the Periodic System. The analogues of oxygen — sulphur, selenium, and tellurium — in group VI, were then taken up. The remaining members of group VI are so distinctly metallic that they will be referred to with the metals. The important members of group V were then studied, and all of the important elements in group IV, with the exception of the metals, tin and lead.

We have begun the study of group III with the first member boron, which is distinctively an acid-forming element. The remaining members of this group, however, are so distinctively base-forming or metallic that they will be studied with the metals.

Having completed our study of the non-metals, or metalloids as they are termed, we shall now turn to the metals, and with these we shall begin with group I — the alkalies.

EXPERIMENTS WITH CARBON, SILICON, AND BORON

Experiment 115. Comparison of the Different Forms of Carbon. — (Graphite; charcoal; bone-black or lamp-black; coal.) Compare the several varieties of carbon; it will be seen that graphite is hard and has crystalline structure. Charcoal and bone-black are soft and without any crystalline form. Certain varieties of coal are hard, while others are quite soft. In general the bituminous coals are soft and the anthracites hard. (See page 190.)

Experiment 116. Absorption of Gases and Coloring-matter by Charcoal. — (Dilute solution of hydrogen sulphide; solution of litmus; bone-black.)

That charcoal will absorb a gas like ammonia was strikingly shown in Experiment 49.

Shake a dilute solution of hydrogen sulphide in water with an excess of bone-black, and filter the solution. Practically all of the hydrogen sulphide will be absorbed by the bone-black, and the solution will be nearly free from the odor of the gas.

Shake a solution of litmus with a considerable quantity of bone-black. Filter. If the solution is not colorless, boil it with more bone-black and again filter. All of the coloring-matter will now be removed from the solution by the bone-black. (See page 191.)

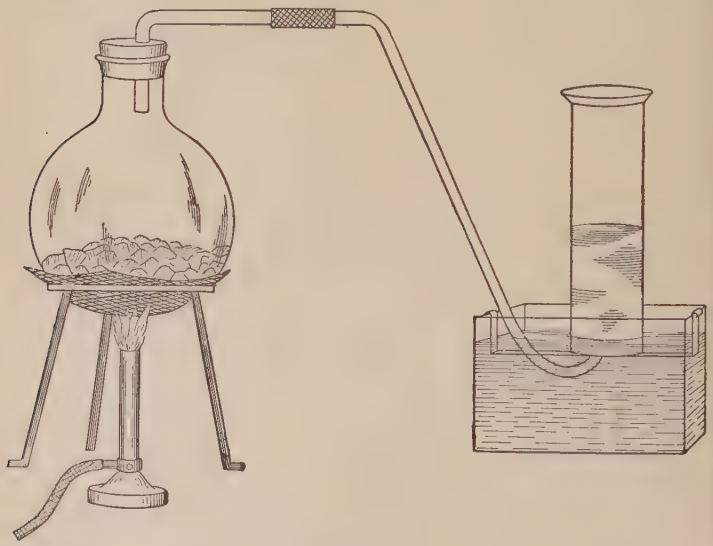

FIG. 53.

Experiment 117. Reducing Power of Carbon. — (Lead oxide; copper oxide.)

Heat a mixture of lead oxide and finely powdered carbon in a hard-glass tube, and conduct any gases which escape into a

solution of barium hydroxide in another test-tube. Insoluble barium carbonate will be formed, showing that the carbon has been oxidized to carbon dioxide. That the zinc oxide has lost oxygen and been reduced to metallic zinc, can be shown by treating the contents of the tube with hydrochloric acid and proving that hydrogen is being evolved.

Perform the same experiments using a mixture of copper oxide and finely divided carbon. (See page 191.)

Experiment 118. Preparation of Methane. — (Jena glass flask holding from 100 to 150 cc.; glass cylinders; trough; fused soda-lime; fused sodium acetate.)

Mix 20 grams of fused soda-lime with 20 grams of fused sodium acetate, and powder the mixture finely. Both substances must be fused to remove the water, which would otherwise be set free during the experiment and break the flask.

Introduce the mixture into the flask and connect the flask with the cylinder as shown in Figure 53. Heat the flask strongly, when an abundance of methane will be given off and can be collected.

When a flame is applied to the mouth of a cylinder filled with methane, combustion will take place. (See page 192.)

Experiment 119. Preparation of Acetylene. — (Calcium carbide.)

A few small pieces of calcium carbide are thrown into a dry test-tube, and a few drops of water carefully added. Smell the escaping gas. Touch a lighted match to the mouth of the test-tube, and the acetylene will burn with a smoky flame. (See page 193.)

The odor of acetylene is observed when a bunsen burner strikes back and burns at the bottom. (See page 193.)

Experiment 120. Carbon Monoxide prepared by Heating Oxalic Acid and Sulphuric Acid. — (Flask holding 500 cc.; thistle-tube; gas wash-bottle; glass tubing; oxalic acid; concentrated sulphuric acid; sodium hydroxide.)

Arrange the apparatus as shown in Figure 54. Into the flask *A*, 20 grams of oxalic acid and 100 grams of concentrated sulphuric acid are introduced. The contents of the flask are gently heated, and the escaping gases — carbon monoxide and carbon dioxide — passed through the wash-bottle *B* containing a solution of caustic soda. The carbon dioxide is absorbed by the alkali, and the carbon monoxide passes on. After the air has been completely driven out of the apparatus, ignite the carbon

monoxide. It burns with a slightly luminous, bluish flame. What is formed when carbon monoxide burns? How would you prove it? (See page 193.)

Experiment 121. Reducing Power of Carbon Monoxide. — (Carbon monoxide generator as in the last experiment; hard-glass tube; oxides of several of the heavy metals, such as iron, copper, zinc, lead, etc.)

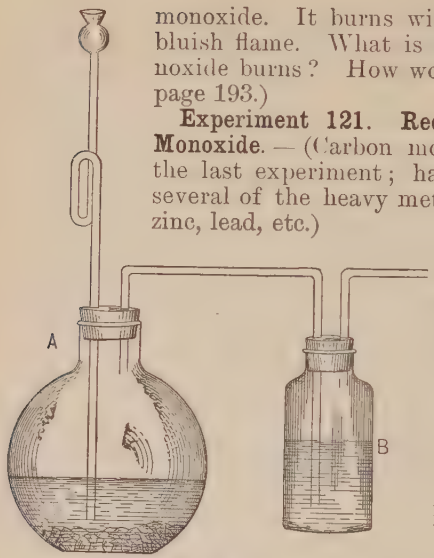

FIG. 54.

Introduce one or more of these oxides at different places in a hard-glass tube resting on a combustion furnace; pass the carbon monoxide through the tube and heat it to a high temperature. Are any of the oxides reduced to the corresponding metal? How do you know? (See page 193.)

Experiment 122. Carbon Dioxide formed by burning Carbon in Oxygen. — (Gasometer filled with oxygen; gas wash-bottle; hard-glass tube; a piece of charcoal; baryta water.)

Introduce a piece of charcoal into a hard-glass tube connected at one end with a gasometer filled with oxygen, and at the other with a gas wash-bottle containing baryta water.

Pass oxygen through the tube and heat the charcoal. It will burn vigorously in the oxygen, and the baryta will become cloudy due to the formation of a precipitate of barium carbonate, showing that carbon dioxide is given off. (See page 194.)

Experiment 123. Carbon Dioxide formed when Magnesite is Heated. — (Hard-glass tube, closed at one end; gas wash-bottle; baryta water; magnesite or marble.)

A small piece of magnesite is introduced into a hard-glass tube, connected with a gas wash-bottle containing baryta water. The magnesite is highly heated, when carbon dioxide escapes and forms a precipitate of barium carbonate. (See page 195.)

Experiment 124. Carbon Dioxide in the Air; in large Quantities in Air exhaled from the Lungs. — (Gas wash-bottle; aspirator as in Figure 34; large test-tube; baryta water.)

By means of an aspirator (Fig. 34) draw air through a gas wash-bottle containing baryta water. Insoluble barium carbonate will gradually be formed.

Close a large test-tube quickly with a two-hole rubber stopper, after introducing a dilute solution of barium hydroxide. Insert one glass tube nearly to the bottom of the test-tube as in Figure 55. A glass tube is introduced into the other hole in the stopper. Air from the lungs is driven through the solution. A heavy precipitate of barium carbonate will quickly form. (See page 195.)

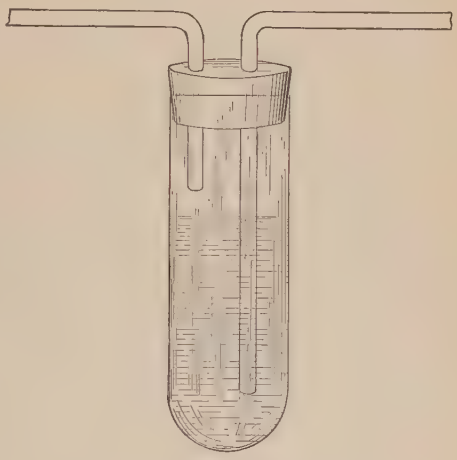

FIG. 55.

Experiment 125. Carbon Dioxide formed by the Action of Acids on Carbonates. — (Sodium carbonate; calcium carbonate; dilute hydrochloric, sulphuric, and nitric acids.)

Treat a few pieces of marble (calcium carbonate) in a test-tube with hydrochloric acid; vigorous action takes place and carbon dioxide escapes.

Perform the same experiment using nitric acid. Similar results are obtained. Treat sodium carbonate in a test-tube with dilute sulphuric acid; carbon dioxide is set free.

Carbon dioxide is *volatile*, and is, therefore, driven out of its salts by other acids. Furthermore, it is a very *weak* acid, and for this reason also would be set free from its compounds by other acids. (See page 195.)

Experiment 126. Preparation of Carbon Dioxide on the Large Scale. — (Kipp apparatus; dilute hydrochloric acid; marble.)

Carbon dioxide is prepared on the large scale by the action of hydrochloric acid on marble. The marble is introduced into the Kipp apparatus (Fig. 8), and also dilute hydrochloric acid. When the gas is desired, it is only necessary to open the stop-cock. When no more gas is wanted, the

stop-cock is closed, and the acid driven automatically off of the marble.

Experiment 127. Carbon Dioxide will not burn and will not support Combustion. — An attempt to ignite carbon dioxide will result in failure. A lighted taper plunged into carbon dioxide will be instantly extinguished. (See page 197.)

Experiment 128. Carbon Dioxide Heavier than Air. — (Large balance sensitively adjusted (Fig. 2); two large beakers; vessel full of carbon dioxide.)

Attach two large beakers to the arms of the large balance (Fig. 2). After the balance has been brought to rest with the pointer in the centre, pour the carbon dioxide into one of the beakers. This arm of the balance will sink. (See page 197.)

Experiment 129. Solid Carbon Dioxide. — (Cylinder containing liquid carbon dioxide; small bag of thick flannel; small porcelain crucible; cotton; mercury.) (*This experiment should be performed only by the instructor.*)

If the cylinder containing the liquid carbon dioxide is slanted so that the liquid runs to the front of the tube, and the valve is carefully opened, some of the carbon dioxide will be volatilized, while a part will be solidified. If the jet is covered with a thick flannel bag, the solid carbon dioxide can be caught, and we have carbon dioxide snow. By means of this substance low temperatures can be produced. Indeed, when mixed with ether, temperatures lower than $-80°$ can be produced.

With solid carbon dioxide mercury can readily be frozen.

Introduce 25 grams of mercury into a small porcelain crucible, resting on a poor conductor of heat such as cotton. Cover the mercury with solid carbon dioxide and cover the crucible. In a short time the mercury will be frozen.

Remove the frozen mercury and plunge it in a vessel containing ice-water. The mercury will become covered with a layer of ice.

Experiment 130. Alcohol formed by the Fermentation of Sugar. — (Balloon flask holding 2 litres; two glass cylinders; condenser; receiver; grape sugar; yeast; barium hydroxide; sodium hydroxide.)

Arrange the apparatus as in Figure 56. Introduce into the flask *A* 100 grams of grape sugar and 1 litre of water. Add yeast, and set in a warm place. Fermentation will soon begin, and carbon dioxide can be collected in cylinder *B*, which contains baryta water, while barium carbonate will be precipi-

tated. The second cylinder *C* contains sodium hydroxide, to protect the baryta from the carbon dioxide in the air.

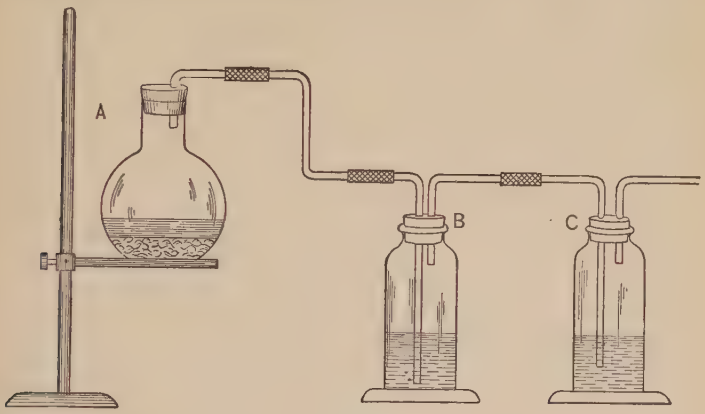

FIG. 56.

After the flask has stood for several days, connect with a condenser as in Figure 15, and distil off the alcohol. The first portion of the distillate will contain a mixture of alcohol and water. The solution will probably contain too little alcohol to take fire and burn when a flame is applied to it.

Fill a test-tube half full of the distillate, and add potassium carbonate and shake until no more will pass into solution. The alcohol, being insoluble in a saturated solution of potassium carbonate, will rise to the surface and appear as a distinct layer floating on the solution. It can be removed by means of a pipette, placed in a small evaporating-dish, and ignited. (See page 198.)

Experiment 131. Carbon Bisulphide, Properties of. — (Small evaporating-dish; bellows; carbon bisulphide.)

That *carbon bisulphide is very inflammable* can be shown by introducing 1 cc. into an evaporating-dish under the hood, and bringing near the dish an ignited gas-lighter. What takes place?

The refrigerating power of carbon bisulphide can be shown by introducing 10 or 15 cc. of the liquid into a test-tube, and covering this with 1 or 2 cc. of water. A current of air from the blast-lamp is blown through the mixture. The carbon bisulphide evaporates so rapidly that the water is frozen. (See page 198.)

Experiment 132. Preparation of Cyanogen. — (Hard-glass tube closed at one end; mercuric cyanide.) (*This experiment should be performed only by the instructor.*)

Mercuric cyanide is introduced into a hard-glass tube closed at one end. The tube is drawn out to a fine tube at the other end. Heat the mercuric cyanide, and cyanogen will be given off. Ignite the jet as it escapes from the tube, and it will burn with the purple flame which is characteristic of the substance. This experiment must be performed only under a good hood, since *cyanogen is very poisonous.* (See page 198.)

Experiment 133. Flames differ greatly in their Luminosity. — (Candle; bunsen burner; fish-tail burner.)

Light a candle, a bunsen burner, and a fish-tail burner. The candle and fish-tail burner are brightly luminous, while the bunsen burner gives very little light. The fish-tale burner and the bunsen burner both use gas, and yet they are markedly different in their light-giving power.

If we examine these burners carefully, we shall find that in the bunsen burner the gas is mixed with air before it reaches the flame, and thus differs from the fish-tail burner. The combustion of the gas is more perfect in the bunsen burner, and the illuminating gas is diluted with an indifferent gas, nitrogen, and hence the lack of luminosity.

If the air is cut off at the base of the bunsen burner, the flame at once becomes luminous. (See page 200.)

Experiment 134. Rendering a Non-luminous Flame Luminous. — (Two bunsen burners; charcoal; platinum cylinder.)

Ignite a bunsen burner, and when it is burning with a practically non-luminous flame, rub together two pieces of carbon near the base of the burner. The fine carbon dust will be drawn into the burner by the current of air, and the flame will become strongly luminous.

Incline a bunsen burner at an angle of 45 degrees, and place a freshly heated platinum tube over the end of the burner. Ignite the gas at the end of the platinum. It will burn with a colorless flame. Now heat the platinum tube to redness with a second burner, and the first flame will become luminous. (See page 201.)

Experiment 135. Use of the Blowpipe. — (Mouth blowpipe; blowpipe tube; a piece of charcoal; several heavy metals such as zinc, lead, etc.; oxides of the heavy metals, such as zinc oxide, cadmium oxide, lead oxide, silver oxide, etc.)

Bore a cavity into the piece of charcoal by means of a coin

placed on its edge and rotated. Place a small piece of metal in the cavity, and heat with the oxidizing flame (the outer tip) of the blowpipe. Describe in each case what occurs? Note any incrustation on the charcoal?

In a similar manner place the oxide of a heavy metal on the charcoal, and heat with the reducing flame of the blowpipe. Does any change take place? Is any metal formed? Try the action of acids on the globule. What occurs? (See page 202.)

Experiment 136. Effect of cooling the Bunsen Flame. — (Bunsen burner; *fine* wire or copper gauze.)

Ignite a bunsen burner and lower a piece of wire gauze upon the flame. The gas will burn beneath the gauze but not above it. The gauze conducts the heat away, and the gas above the gauze is not ignited. After a time the gauze becomes sufficiently hot to ignite the gas above it. Apply a match to the gas above the gauze; it will ignite.

Turn the gas on a bunsen burner and do not ignite the gas. Bring the wire gauze about 5 cm. above the burner, and ignite the gas above the gauze with a match. It will burn above the gauze while no flame will appear below the gauze. (See page 203.)

Experiment 137. Preparation of Silicon Dioxide. — (Water-glass; hydrochloric acid.)

Treat a little water-glass with hydrochloric acid. Filter off the precipitate, wash, dry, and ignite in a porcelain crucible. The product is silicon dioxide. (See page 205.)

Experiment 138. Formation of a Salt of Silicic Acid. — (Sand; porcelain or nickel crucible; sodium carbonate.)

Powder a little sand in a porcelain mortar until it is a mere dust. Mix it with ten times its volume of sodium carbonate, and introduce the mixture into the porcelain or nickel crucible. Heat over a blast-lamp for ten minutes. The mass will then dissolve in water. To the solution of sodium silicate add hydrochloric acid. What is precipitated? (See page 206.)

Experiment 139. Preparation of Boric Acid; Color imparted to the Alcohol Flame. — (Borax; concentrated hydrochloric acid; alcohol.)

Dissolve 50 grams of borax in 200 cc. of water, and add concentrated hydrochloric acid until the solution is strongly acid to litmus. When the solution cools, boric acid crystallizes out.

Dissolve a few crystals of the boric acid in a little alcohol, pour the solution into an evaporating-dish and ignite the alcohol. It will burn with a characteristic greenish flame.

Compare this flame with that produced by burning pure alcohol. (See page 208.)

PROBLEMS

1. Amount of carbon in 3 grams of methane? in 3 grams of ethylene? in 3 grams of acetylene?
2. What weight of carbon dioxide would be produced by burning a diamond weighing 0.5 grams?
3. Quantity of ethyl alcohol required to contain 1 gram of carbon?
4. Weight of carbon bisulphide which could be formed from 1 kilogram of graphite and sulphur; how much sulphur would be used up?
5. When 3.3 grams of mercuric cyanide are heated, what would be the weight of the cyanogen set free?
6. Amount of silicon in 7.3 grams of quartz?
7. Weight of boron trioxide in 100 grams of borax?

CHAPTER XVIII

THE METALS

The metals have certain properties in common which distinguish them from the other elements. With one exception, they are all solids at ordinary temperatures.

Some of the metals, like sodium, potassium, etc., are very active chemically, while others, like platinum, gold, etc., are very resistant to chemical reagents.

The chemistry of the metals is in general much simpler than that of the metalloids. The metals form ions charged with positive electricity, — *cations*, — and these combine with the anions of acids, forming salts. The cations are generally very much simpler than the anions, consisting usually of single metal atoms charged with positive electricity.

Since when metals react chemically they pass into solution, *i.e.* into the ionic state, the study of the chemistry of the metals is largely the study of the ions which they form. Indeed, we have excellent reason for believing that in order that the metals should react chemically they must be in the ionic state. If this be true, the *study of the chemistry of the metals is in reality a study of them in the ionic condition.*

We shall take up first the alkali metals, consisting of lithium, sodium, potassium, rubidium, and cæsium.

Next in order come the metals of group II. These fall, with respect to their relationships, into two divisions, — calcium, strontium, and barium, on the one hand; and glucinum, or beryllium magnesium, zinc, cadmium, and mercury, on the other.

When we pass to group III, we find that boron has already

been studied with the metalloids. The first metal in this group is aluminium. In the same group are the rare elements, scandium, gallium, yttrium, indium, lanthanum, ytterbium, thallium, and samarium.

Passing to iron, we have in this same group nickel, cobalt, manganese, chromium, and the rarer elements, molybdenum, tungsten, and uranium.

Next are taken up copper, silver, and gold, and then lead and tin; the former appearing in group I, the latter in group IV.

Finally, among the noble metals, we have rhodium, ruthenium, palladium, osmium, iridium, and platinum.

THE ALKALI METALS

LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, AND CÆSIUM

SODIUM (At. Wt. = 23.05)

Occurrence of the Element Sodium. — The element sodium is very widely distributed, and occurs in combination with other elements in many places in large quantities. On account of its great chemical activity it does not occur in nature in the free condition. Nearly all of the salts of sodium are soluble in water. We should, therefore, expect to find most of the sodium compounds dissolved in the waters of the sea, and such is the fact.

In certain arid regions one of the most soluble salts of sodium exists in large beds. In Chili, large beds of sodium nitrate are found which, from their analogy to potassium nitrate or ordinary saltpetre, are known as *Chili saltpetre.*

Sodium salts exist in great abundance in certain regions where the waters of the sea have evaporated. In the great salt beds of the earth, such as those at Stassfurt, the chloride and other compounds of sodium occur. One compound of sodium which has recently come into prominence in connection

with the manufacture of aluminium should be mentioned. This is the double fluoride of sodium and aluminium, Na_3AlF_6, occurring in Greenland and known as *cryolite*.

Preparation of Sodium.— Sodium was prepared for a long time by the reduction of the oxide or hydroxide by means of metallic magnesium, or by highly heated carbon.

All of these reduction methods are now abandoned when it is desired to prepare sodium on a large scale. The electrolytic method is used entirely.

Sodium prepared by the electrolysis of the fused hydroxide is not an expensive substance, the price having been reduced immensely by the application of the electrolytic process.

Properties of Metallic Sodium. — Sodium is a soft solid, which, when freshly cut with a knife, has a metallic lustre and a steel-gray color. The surface becomes quickly tarnished, due to the rapidity with which it takes up oxygen from the air or from moisture, forming the oxide or hydroxide. In the presence of water the following reaction takes place: —

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2.$$

The hydrogen which is liberated when a piece of sodium is thrown upon water, does not take fire if the sodium is allowed to move about over the surface of the water. If the sodium is held in one place, as by throwing it upon a piece of filter-paper upon the water, enough heat is produced to ignite the hydrogen.

Sodium Hydride, NaH, is formed when metallic sodium is heated to 300° in a current of hydrogen.

Sodium Peroxide, NaO. — As far as is known with certainty, sodium forms only one compound with oxygen. This is the peroxide NaO. It is obtained when sodium is heated in the atmosphere to about 300° to 350°. It is a light yellow powder, and dissolves readily in water, forming sodium hydroxide and hydrogen dioxide. The reaction would be represented thus: —

$$2\,NaO + 2\,H_2O = 2\,NaOH + H_2O_2.$$

Sodium Hydroxide, NaOH. — We have just seen that one method of preparing sodium hydroxide is to treat the peroxide with water. Sodium hydroxide is now prepared on the large scale by the electrolysis of sodium chloride. Still another method is to treat sodium carbonate with calcium hydroxide: —

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2\,NaOH.$$

Another method, and perhaps the best, for preparing a little sodium hydroxide in very pure condition is to allow water to act on metallic sodium: —

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2.$$

On account of the violence of this reaction it must be carried out with certain precautions.

Sodium hydroxide is one of the strongest bases known. When brought into the presence of water, it dissociates thus: —

$$NaOH = \overset{+}{Na},\ \overset{-}{OH}.$$

When sodium hydroxide is treated with hydrochloric acid, they react as follows: —

$$\overset{+}{Na},\ \overset{-}{OH} + \overset{+}{H},\ \overset{-}{Cl} = \overset{+}{Na},\ \overset{-}{Cl} + H_2O.$$

The Chemistry of Sodium the Chemistry of the Sodium Ion. — The chemistry of the element sodium is not the chemistry of the atom or molecule of sodium, since there is every reason for believing that these are practically inert.

On the other hand, wherever we have sodium ions present, we have the reactions which are characteristic of this element. Some of these reactions, together with their products, we shall now study.

Sodium Chloride is found in great abundance in sea-water, which, on the average, contains about 2.7 per cent of the salt. The amount of sodium chloride in sea-water, however, varies greatly from one locality to another. In tropical regions, where the evaporation of the water is relatively rapid, the percentage may be as much as 3.5 to 3.8 per cent.

The salt is obtained from sea-water by evaporation. The water is allowed to flow into shallow pools, and be evaporated by the heat of the sun.

On account of its abundance and cheapness, sodium chloride is of great importance as a source of both chlorine and sodium.

Sodium bromide, NaBr, and *sodium iodide*, NaI, resemble the chloride so closely in their properties that a detailed study of them in this connection is not necessary.

Sodium Nitrate, $NaNO_3$. — Sodium nitrate is called *Chili saltpetre*, because it is found in a certain rainless district in Chili, and since it is the sodium analogue of potassium nitrate or ordinary saltpetre. It is extremely soluble in water, and, therefore, could not exist in the solid condition in regions where there is appreciable rainfall.

Sodium nitrate cannot be used in making gunpowder in the place of potassium nitrate, since it absorbs water from the air, or is *deliquescent*, as we say.

Sodium Sulphate, $Na_2SO_4 . 10\,H_2O$. — Sodium sulphate, called from its discoverer, *Glauber's salt*, exists in certain mineral waters as those of Carlsbad. It is formed in a large number of reactions. When sulphuric acid is neutralized with sodium hydroxide, we have: —

$$2\,NaOH + H_2SO_4 = 2\,H_2O + Na_2SO_4.$$

When sodium chloride is treated with sulphuric acid, sodium sulphate is formed, not because sulphuric acid is as strong as hydrochloric, but because the latter is volatile: —

$$2\,NaCl + H_2SO_4 = 2\,HCl + Na_2SO_4.$$

Acid Sodium Sulphate, $NaHSO_4$. — Acid sodium sulphate is formed by the action of sulphuric acid on salts of sodium with volatile acids: —

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

Also by the action of sulphuric acid on the neutral sulphate: —

$$Na_2SO_4 + H_2SO_4 = 2\,NaHSO_4.$$

When carefully heated in a vacuum to 300°, it loses water and forms the *pyrosulphate* : —

$$2\,NaHSO_4 = H_2O + Na_2S_2O_7.$$

Sodium Thiosulphate, $Na_2S_2O_3 . 5\,H_2O$. — This salt is frequently referred to as sodium hyposulphite, or in commerce simply as "hypo." It is prepared by dissolving sulphur in a solution of sodium sulphite: —

$$Na_2SO_3 + S = Na_2S_2O_3.$$

Solutions of this salt dissolve silver chloride and bromide, and it is, therefore, used to remove these substances from the photographic plate after the plate has been exposed to the light.

Sodium Carbonate, $Na_2CO_3 . 10\,H_2O$. — The salt with ten molecules of water crystallizes from a solution allowed to cool on the air. This salt loses a part of its water at ordinary temperatures — is *efflorescent.*

The Le Blanc Method for preparing sodium carbonate was used almost exclusively until quite recently. In the Le Blanc method the sodium chloride is converted into the sulphate by means of sulphuric acid. The sulphate is reduced to the sulphide by means of highly heated carbon, the sulphide heated with calcium carbonate, when, at a sufficiently high temperature, calcium sulphide and sodium carbonate are formed. The reactions expressing these three transformations are: —

I. $$2\,NaCl + H_2SO_4 = 2\,HCl + Na_2SO_4,$$

II. $$Na_2SO_4 + 4\,C = 4\,CO + Na_2S,$$

III. $$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

It is not difficult to separate the sodium carbonate from the calcium sulphide, since the latter is difficultly soluble in water, while sodium carbonate is readily soluble.

The Solvay or Ammonia Process is based upon the fact that acid sodium carbonate is much less soluble in water than acid

ammonium carbonate. Ammonia and sodium chloride are dissolved in water, and carbon dioxide passed into the mixture.

Under these conditions acid sodium carbonate, on account of its small solubility, separates from the solution. The reactions may be represented thus: —

$$NH_3 + H_2O + CO_2 = NH_4HCO_3,$$
$$NH_4HCO_3 + NaCl = NH_4Cl + NaHCO_3.$$

The acid sodium carbonate when heated forms the normal carbonate, carbon dioxide, and water: —

$$2\,NaHCO_3 = H_2O + CO_2 + Na_2CO_3.$$

The carbon dioxide is conducted into more ammonia in the presence of sodium chloride, and the process is thus a continuous one.

Acid Sodium Carbonate, $NaHCO_3$. — Primary sodium carbonate, or acid sodium carbonate, or the "bicarbonate of soda," is formed by the action of carbon dioxide on the normal carbonate: —

$$Na_2CO_3 + CO_2 + H_2O = 2\,NaHCO_3.$$

It is also formed, as we have just seen, in the preparation of normal sodium carbonate by the ammonia process. When acid ammonium carbonate, formed by the action of carbon dioxide on ammonia, is treated with sodium chloride, acid sodium carbonate is formed: —

$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

Hydrolysis of the Carbonates. — The aqueous solution of normal sodium carbonate has a strongly alkaline reaction. Indeed, the primary or acid carbonate has a weakly alkaline reaction. This is due to the presence of hydroxyl ions in the aqueous solutions of the carbonates. The carbonates are salts of the very weak carbonic acid, and like all salts of weak acids are *hydrolyzed* to a greater or less extent by water: —

$$Na_2CO_3 + H_2O = \overset{+}{N}a,\ \overset{-}{O}H + \overset{+}{N}a,\ \overset{-}{H}CO_3.$$

Even the acid carbonate is hydrolyzed to a sufficient extent to show an alkaline reaction.

All carbonates which are soluble in water are hydrolyzed sufficiently to show an alkaline reaction.

The Phosphates of Sodium. — Since phosphoric acid is tribasic (see phosphorus), there are three sodium salts of this acid possible, and all are known. The *secondary sodium phosphate*, Na_2HPO_4, is by far the best known, and is always meant when the term "sodium phosphate" is used without qualification. It contains twelve molecules of water of crystallization.

Its aqueous solution is slightly alkaline, due to the fact that phosphoric acid is a weak acid, and it is slightly hydrolyzed by water: —

$$Na_2HPO_4 + H_2O = \overset{+}{N}a,\ \overset{-}{O}H + \overset{+}{N}a,\ H_2\overset{-}{P}O_4.$$

When disodium phosphate is treated with one equivalent of phosphoric acid, the *monosodium phosphate*, NaH_2PO_4, is formed: —

$$Na_2HPO_4 + H_3PO_4 = 2\,NaH_2PO_4.$$

If, on the other hand, one equivalent of sodium hydroxide is added to one equivalent of disodium phosphate, the *trisodium phosphate* is formed: —

$$Na_2HPO_4 + NaOH = Na_3PO_4 + H_2O.$$

Sodium Borate or Tetraborate, $Na_2B_4O_7 \cdot 10\,H_2O$. — Borax is not the salt of normal boric acid, H_3BO_3, but of a polyboric acid, derived from the normal acid by loss of water. When four molecules of boric acid lose five molecules of water, the acid from which borax is formed results: —

$$4\,H_3BO_3 = 5\,H_2O + H_2B_4O_7.$$

Borax, or sodium tetraborate, is formed when boric acid is neutralized with sodium carbonate: —

$$4\,H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6\,H_2O + CO_2.$$

On account of the property of dissolving metal oxides borax is frequently used as a *flux*. It is used for the same reason to

clean two metal surfaces which it is desired to *solder* together. These usually become covered with a layer of oxide when the metal is heated, and the solder will not adhere to the surfaces while the oxide is present. When a little borax is added, it removes at the elevated temperature the oxides already formed, and at the same time protects the hot metal surfaces from the oxygen of the air.

POTASSIUM (At. Wt. = 39.14)

Occurrence and Preparation. — Potassium like sodium does not occur in nature in the free condition, and for the same reason, viz. its great chemical activity.

Plants have the power of taking up potassium ions in large quantities and building them up into their tissues. When such plants are burned the potassium salts remain behind in the ashes.

Potassium also occurs in many of the more common rocks and minerals in the form of silicates. Ordinary *feldspar* is a double silicate of potassium and aluminium.

Potassium salts also occur in the great salt beds, especially in those of Stassfurt, in Germany.

Potassium was prepared by reducing the sulphide or hydroxide with highly heated metals, such as magnesium, aluminium, iron, etc.

All of these methods have now been abandoned in favor of the electrolytic. Metallic potassium is now prepared by electrolyzing the chloride, or hydroxide.

Properties of Potassium. — Potassium is characterized by its great chemical activity, being even more active than sodium. When a small piece of potassium is thrown upon water, it decomposes it in the same manner as sodium, yielding potassium hydroxide and setting hydrogen free: —

$$2\,H_2O + 2\,K = 2\,KOH + H_2.$$

The action in the case of potassium is, however, so vigorous that even when the metal is allowed to move around over the

surface of the water, enough heat is generated to ignite the hydrogen.

Potassium Hydride, KH, is formed when potassium is heated to 300° — 400° in a current of hydrogen.

Potassium Peroxide, KO_2. — The only compound which potassium is known to form with oxygen is the dioxide. It is obtained by heating potassium in a current of dry oxygen. It is an orange-colored powder, melting at 280°. In contact with water it forms potassium hydroxide, hydrogen dioxide, and oxygen: —

$$2\,KO_2 + 2\,H_2O = 2\,KOH + H_2O_2 + O_2.$$

Potassium Hydroxide, KOH. — When metallic potassium is thrown upon water, potassium hydroxide is formed, as we have seen.

It is also formed when the peroxide is dissolved in water.

When a concentrated, aqueous solution of potassium chloride is electrolyzed, potassium hydroxide is formed in the solution.

Potassium hydroxide dissolves very readily in water, forming *caustic potash*, and the solution is one of the strongest bases known. It dissociates completely into potassium and hydroxyl ions, —

$$KOH = \overset{+}{K},\ \overset{-}{OH},$$

and this at no very great dilution. It is also formed by the action of lime-water on potassium carbonate: —

$$K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2\,KOH.$$

Potassium hydroxide, on account of its great solubility, readily precipitates the hydroxides of the heavy metals from aqueous solutions of their salts: —

$$\overset{+}{Ag}\overset{-}{NO_3} + \overset{+}{K},\ \overset{-}{OH} = AgOH + \overset{+}{K},\ \overset{-}{NO_3}.$$

Silver hydroxide, however, breaks down into silver oxide and water.

Potassium Chloride, KCl, occurs in nature as such, in combination with magnesium chloride as the mineral *carnallite*, $KMgCl_3 . 6\,H_2O$, and in other combinations. When a hot

solution of this salt crystallizes, the double salt decomposes, potassium chloride separating out. It is a beautifully white substance, crystallizing in cubes, which are readily dissolved by water. Potassium chloride is a type of a salt of a strong acid with a strong base. We have seen that strong acids and strong bases mean those that are greatly dissociated. The compound formed by the union of the cation of the base, $\overset{+}{K}$, with the anion of the acid, $\overset{-}{Cl}$, is among the most strongly dissociated substances known. A dilute solution of potassium chloride is, therefore, a solution of potassium and chlorine ions and nothing else, there being no molecules in the solution. All the properties of such solutions, both chemical and physical, are the properties of chlorine ions and potassium ions, since these only are present. The bromide, iodide, and fluoride of potassium resemble closely the chloride.

Potassium Chlorate, $KClO_3$.— Potassium combines with the oxygen acids of chlorine, forming well-defined salts. A few of these are of sufficient importance to merit special consideration. Potassium chlorate is prepared, as we have seen, by the action of chlorine on caustic potash: —

$$6\,KOH + 3\,Cl_2 = 5\,KCl + KClO_3 + 3\,H_2O.$$

It is separated from the chloride by its solubility in water being much less than that of the chloride.

When potassium chlorate is heated, it decomposes in the sense of the following equation, —

$$2\,KClO_3 = KCl + KClO_4 + O_2,$$

potassium chloride and perchlorate being formed. When the perchlorate is heated to a still higher temperature, it breaks down into the chloride and oxygen.

When potassium chlorate is powdered with a small piece of sulphur, an explosion occurs, which is violent if an appreciable quantity of sulphur is used. A violent explosion results if potassium chlorate is brought together with phosphorus. With antimony sulphide an explosive mixture is also formed.

Potassium chlorate is extensively used in the preparation of matches. The so-called *safety matches* are made of a mixture of potassium chlorate and sulphide of antimony. When these are rubbed upon a surface covered with red phosphorus, a miniature explosion results and the whole mass is ignited. When rubbed upon an ordinary object such matches do not take fire.

Potassium Nitrate, KNO_3. — Potassium nitrate or saltpetre is one of the most important salts of potassium. It is very soluble in water and, therefore, does not occur in the solid state in any considerable quantity in regions where there is an abundant rainfall.

Potassium nitrate is formed in large quantity in the *saltpetre plantations*. Refuse animal matter which contains nitrogen is mixed with potassium carbonate, and exposed to the action of the *nitrifying ferment* or *saltpetre bacteria* in the soil. The oxygen of the air, through the agency of these bacteria, oxidizes the ammonia formed from the decomposing organic matter, to nitric acid, which then combines with potassium hydroxide or carbonate and forms the corresponding nitrate.

Potassium nitrate is made to-day chiefly from sodium nitrate or Chili saltpetre. When a solution of sodium nitrate is mixed with a solution of potassium chloride, the following reaction takes place: —

$$\overset{+}{\mathrm{Na}}, \overset{-}{\mathrm{NO}_3} + \overset{+}{\mathrm{K}}, \overset{-}{\mathrm{Cl}} = \mathrm{NaCl} + \overset{+}{\mathrm{K}}, \overset{-}{\mathrm{NO}_3}.$$

The sodium chloride is deposited at higher temperatures. When the solution is allowed to cool down, potassium nitrate is deposited. *Gunpowder* is a mixture of potassium nitrate, sulphur, and carbon, in such proportions as to secure complete combustion. The nitrate gives off oxygen, which combines with the carbon, forming carbon dioxide; the nitrogen escapes as such, and the potassium remains behind in the form of the sulphide or sulphate. The equation which is usually written to express the decomposition of gunpowder is: —

$$2\,\mathrm{KNO_3} + 3\,\mathrm{C} + \mathrm{S} = \mathrm{K_2S} + 3\,\mathrm{CO_2} + \mathrm{N_2}.$$

Gunpowder is prepared by mixing the three constituents in the following proportions: —

KNO_3	75 per cent
S	12 per cent
C	13 per cent

This corresponds almost exactly to three molecules of saltpetre, three atoms of carbon, and one atom of sulphur; and is the chief reason for writing the above very simple equation.

When gunpowder is ignited, the gases liberated occupy several hundred times the volume of the powder; or if they are forced to occupy the same volume as the original powder, the pressure exerted is several hundred atmospheres. This is the principle made use of in employing explosives to drive missiles with a high velocity. The gunpowder is exploded in a metal tube closed on all sides and open at one end. The ball is placed tightly upon the powder, so that when the latter explodes the gases are liberated in practically a closed space. An enormous pressure is thus generated, which drives the ball out of the end of the gun with a high velocity.

Potassium Sulphate, K_2SO_4, occurs in nature in combination with magnesium sulphate and magnesium chloride as *kainite*. It occurs in a number of the salt beds, but especially in those at Stassfurt and other places in Germany. Kainite has the composition $K_2SO_4 . MgSO_4 . MgCl_2 . 6\,H_2O$. The double sulphate of potassium and magnesium is treated with chloride of potassium, when magnesium chloride and potassium sulphate result.

When normal potassium sulphate is treated with an equivalent of sulphuric acid, the *acid, or primary sulphate,* is formed: —

$$K_2SO_4 + H_2SO_4 = 2\,KHSO_4.$$

Acid potassium sulphate in aqueous solution shows a strongly *acid reaction*. This is due to the fact that sulphuric acid is a strong acid, and the hydrogen of the acid sulphate begins to dissociate:

$$KHSO_4 = \overset{+}{K}, \overset{+}{H}, \overset{=}{SO_4}.$$

Potassium Carbonate, K_2CO_3. — Potassium carbonate was obtained for a long time mainly from the ashes of certain plants. When the plants were burned, the potassium remained behind in the form of the carbonate. This was obtained by leaching the ashes with water and evaporating the solution, when the impure carbonate crystallized out. Potassium carbonate is also obtained from the residues of the beet-sugar industry.

The carbonate is purified by means of the difference in solubility between the impurities and the salt in question.

Acid, or Primary Potassium Carbonate, $KHCO_3$. — The acid salt is formed by conducting carbon dioxide into the solution of the neutral salt: —

$$K_2CO_3 + CO_2 + H_2O = 2\,KHCO_3.$$

Dilute solutions of acid potassium carbonate react alkaline. This is due to the hydrolysis of the acid salt by water, forming hydroxyl ions: —

$$KHCO_3 + H_2O = \overset{+}{K},\ \overset{-}{OH} + H_2CO_3.$$

Phosphates of Potassium. — Potassium, like sodium, forms three salts with phosphoric acid, — the primary, KH_2PO_4; secondary, K_2HPO_4, and tertiary, K_3PO_4, phosphates.

These phosphates do not call for any special comment.

The elements *lithium*, *rubidium*, and *cæsium* are comparatively rare elements which need not be considered in detail.

AMMONIUM

The group ammonium, although not an element, closely resembles in its properties the alkali metals. It forms a univalent cation, $\overset{+}{N}H_4$, which has the power to combine with the anions of acids and form salts which resemble in many respects those of the alkali metals.

Ammonium Hydroxide, NH_4OH. — Ammonia combines with water, forming the hydroxide NH_4OH: —

$$NH_3 + H_2O = NH_4OH.$$

In the presence of water this compound is dissociated to some extent into the ammonium ion, $\overset{+}{N}H_4$, and the hydroxyl ion, $\overset{-}{O}H$: —

$$NH_4OH = \overset{+}{N}H_4, \overset{-}{O}H.$$

It is, therefore, a base, but it is a very weak base.

When an aqueous solution of ammonium hydroxide is boiled, it breaks down into ammonia and water: —

$$NH_4OH = NH_3 + H_2O.$$

This fact is made use of in detecting the presence of ammonia or an ammonium salt. The ammonium salt is treated with a strong base like caustic soda, when it is broken down into the sodium salt, and ammonia which is given off when the solution is heated. This can be detected by the odor when present in considerable quantity, or by holding a piece of moistened red litmus in the escaping vapors when the ammonia is present in small quantity. This becomes colored blue.

Ammonium Chloride, NH_4Cl. — When hydrochloric acid is neutralized with ammonium hydroxide and the solution evaporated, ammonium chloride or *sal ammoniac* is obtained. This salt is a beautifully crystalline compound, which is readily soluble in water. Although ammonium hydroxide is only slightly dissociated, the salt with hydrochloric acid is among the most strongly dissociated compounds. This is true in general of the salts of ammonia with strong acids.

Ammonium Hydrosulphide, Sulphide, and Polysulphides. — When a solution of ammonium hydroxide is saturated with hydrogen sulphide, the *hydrosulphide*, NH_4HS, is produced: —

$$NH_4OH + H_2S = H_2O + NH_4HS.$$

The *sulphide of ammonium*, $(NH_4)_2S$, is formed by treating the hydrosulphide in solution with an equivalent of ammonia: —

$$NH_4HS + NH_4OH = (NH_4)_2S + H_2O.$$

The aqueous solution of ammonium sulphide is colorless when freshly prepared, but when allowed to stand for a time

it becomes deep yellow in color. This is due to the oxidation of the sulphide by the oxygen of the air setting sulphur free: —

$$(NH_4)_2S + O = H_2O + 2\,NH_3 + S.$$

The sulphur thus set free acts on more ammonium sulphide, forming the polysulphides of ammonium. There are several of these compounds.

Ammonium Sulphate, $(NH_4)_2SO_4$. — This is one of the most important salts of ammonia, as being one of the chief sources of the ammonia used on a commercial scale.

Ammonium Carbonate, $(NH_4)_2CO_3 . H_2O$. — When a mixture of calcium carbonate and ammonium sulphate is distilled, and ammonia passed into the aqueous solution of the product, normal ammonium carbonate is formed. This is not very stable, and breaks down readily into ammonia and the *acid carbonate*, NH_4HCO_3: —

$$(NH_4)_2CO_3 = NH_3 + NH_4HCO_3.$$

The acid carbonate is also formed by the action of carbon dioxide on aqueous ammonia. This is a much more stable substance than the normal carbonate.

The Double Phosphate of Ammonium and Sodium. — The double phosphate of ammonium and sodium, $NaNH_4HPO_4$, or *microcosmic* salt, is formed by bringing together, in solution, disodium phosphate and ammonium chloride: —

$$Na_2HPO_4 + NH_4Cl = NaCl + NH_4NaHPO_4.$$

When heated it decomposes into ammonia, water, and sodium metaphosphate: —

$$NH_4NaHPO_4 = NH_3 + H_2O + NaPO_3.$$

Characteristics of the Alkali Metals in General. — From the foregoing study of the alkalies we can draw general conclusions as to their chemical behavior. In the first place, they are all *strongly base-forming elements*, which is the same as to say that when they are dissolved in water they form strongly electropositive cations, there being a corresponding number of hydroxyl anions present in the solution.

The alkalies form only *univalent ions*, which means that they can carry only one electrical charge.

EXPERIMENTS WITH SODIUM POTASSIUM AND AMMONIUM

Experiment 140. Properties of Sodium. — (Small piece of metallic sodium.)

Remove with forceps a piece of metallic sodium the size of a pea from the bottle containing sodium covered with kerosene. Dry it by pressing between layers of filter-paper. *Do not touch metallic sodium with the hand.*

Holding the sodium in a pair of forceps, cut it with a dry knife. What is the appearance of the surface? Does it change? Why?

Throw a piece of sodium the *size of a grain of rice* on water in an evaporating-dish. What do you observe?

Lay a piece of filter-paper on the water, and when it is wet throw a piece of sodium on the paper. The hydrogen takes fire. Why? (See page 221.)

Experiment 141. Properties of Sodium Hydroxide. — (Sodium hydroxide.)

Dissolve sodium hydroxide in water in which a thermometer is immersed. Is there any change in the temperature? Test the reaction towards red litmus? What is formed when sodium hydroxide is neutralized with acids? (See page 222.)

Experiment 142. Preparation of Sodium Carbonate by the Ammonia or Solvay Process. — (Ammonia; sodium chloride; carbon dioxide generator.)

Make a fairly concentrated solution of sodium chloride in 100 cc. of aqueous ammonia. Pass carbon dioxide into the solution until no more is absorbed. A white precipitate is formed. Dry the compound and then place a little in a hard-glass tube closed at one end, and connected with a bottle containing baryta water. Heat the compound. Is carbon dioxide given off?

When the gas ceases to escape, remove the residue and treat it with an acid. Is carbon dioxide given off? Explain why all the carbon dioxide was not driven off by heat. Write the equations for all of the above reactions? (See page 225.)

Experiment 143. Potassium Hydroxide precipitates the Hydroxide of the Heavy Metals. — (Ferric chloride; lead nitrate; nickel chloride; copper chloride.)

Make dilute solutions of the above-named salts in water, and add a few drops of potassium hydroxide to each solution. Describe in each case what you see?

Sodium hydroxide will answer just as well as potassium hydroxide. (See page 228.)

Experiment 144. Quantitative Determination of Oxygen in Potassium Chlorate. — (Hard-glass tube 8 mm. in diameter, closed at one end; burette, Figure 58; potassium chlorate.)

Fig. 57.

Weigh a hard-glass tube of about 8 mm. internal diameter, and 12 cm. long, closed at one end. Introduce about 0.2 gram of potassium chlorate, and reweigh the tube and chlorate so as to ascertain the exact weight of the chlorate in the tube. Introduce a plug of freshly heated asbestos and shove it down upon the chlorate in the tube. This will sweep down any chlorate adhering to the walls of the tube.

Draw the tube out as shown in the figure (57).

Attach to a burette of the form shown in Figure 58, after filling the tubes nearly full of water. Bring the water to the same level in the two arms of the burette and read the burette.

Now heat the potassium chlorate until all of the oxygen has been driven off. Allow the gas to stand in the burette until it has come to the same temperature as the air in the room. Read the burette again after bringing the water in both arms to the same level. Also read a thermometer suspended from the top of the burette, and a barometer, in the same room.

Correct the observed volume of the gas according to the equation, page 112. Knowing the weight of a litre of oxygen (1.4296 grams), calculate the weight of the oxygen obtained.

Calculate the weight of the oxy-

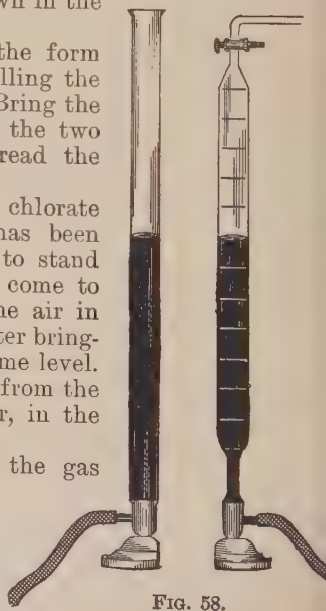

Fig. 58.

gen which should be given off by the potassium chlorate used. Compare the two results. (See page 229.)

Experiment 145. Potassium Nitrate mixed with Carbon readily burns. — (Charcoal; potassium nitrate.)

Powder 3 grams of charcoal in a mortar, and mix intimately with it 18 grams of powdered potassium nitrate. Place the mixture in a metal pan and ignite it with the flame of a bunsen burner. What takes place? (See page 230.)

Experiment 146. Volatility of Ammonium Salts. — (Evaporating-dish; porcelain triangle; ammonium chloride, sulphate, nitrate, and carbonate.)

Place a small porcelain evaporating-dish on a porcelain triangle on a tripod, and introduce one of the above salts. Heat, and it completely volatilizes. Perform the same experiment with the other salts. (See page 233.)

Experiment 147. Formation of Ammonium Sulphide and Ammonium Hydrosulphide. — (Ammonia; hydrogen sulphide.)

Divide 100 cc. of aqueous ammonia into two equal parts. Saturate one-half with hydrogen sulphide. What is formed? Add the other half. What is formed? (See page 233.)

Experiment 148. Ammonium Sulphide precipitates the Sulphides of the Heavy Metals. — (Solution of ammonium sulphide; solution of lead nitrate, cadmium chloride, zinc chloride, mercuric chloride, silver nitrate.)

Add ammonium sulphide to solutions of each of the above substances. Describe in each case what you observe? (See page 233.)

Experiment 149. General Flame Reactions of Sodium and Potassium. — (Salts of sodium; salts of potassium; ammonium salts; hydrofluosilicic acid; perchloric acid; hydrochlorplatinic acid; tartaric acid; 4 platinum wires each 10 cm. long.)

Dip a platinum wire into hydrochloric acid and then heat in a bunsen flame until it no longer imparts color to the flame. Then dip the wire into any sodium salt and thrust it into the flame. How does sodium affect the flame?

Dip another clean platinum wire into any potassium salt and thrust it into the flame. What color does potassium impart to the flame?

Mix a potassium salt with a sodium salt and dip a clean platinum wire into the mixture. The yellow sodium light being so intense, the purple due to the potassium may not be seen. Hold between the eye and the flame a piece of blue

cobalt glass. This will cut off the yellow light due to the sodium, and then the purple potassium flame can be readily seen. This is a convenient means of distinguishing between sodium and potassium, and of detecting each in the presence of the other when both are present.

Ammonium salts do not give any characteristic color to the flame.

PROBLEMS

1. Weight and volume of hydrogen that would be liberated when 2 grams of sodium act on water? What amount of sodium chloride could be produced from the sodium hydroxide formed?

2. How much sodium sulphate would be formed when 500 grams of sodium chloride are treated with sulphuric acid?

3. Percentage of potassium, oxygen, and nitrogen in potassium nitrate?

4. From 7.3 grams of microcosmic salt how much sodium metaphosphate can be obtained?

CHAPTER XIX

THE ALKALINE EARTHS

CALCIUM, STRONTIUM, BARIUM

CALCIUM (At. Wt. = 40.1)

The metals which we have thus far studied are all univalent, or their ions carry one electrical charge each. In the second group of the metals the ions are nearly always bivalent, and in the calcium, strontium, barium sub-group they are always bivalent. The salts which these elements form with the anions of acids are of the general type MCl_2, $M(NO_3)_2$, MSO_4, and so on. With this conception in mind we may now proceed to study some of the compounds formed by the several members of the group.

Occurrence, Preparation, and Properties of Calcium. — Calcium occurs very widely distributed in nature and in large quantities. The carbonate occurs in great abundance as *marble* if well crystallized and pure, or if impure as *limestone* or *chalk*. If in combination with magnesium carbonate, we have *dolomite*. Calcium phosphate occurs in considerable quantity in certain phosphate beds. *Gypsum*, or calcium sulphate, occurs in considerable quantity, while calcium fluoride, or *fluor-spar*, exists in certain localities. Calcium comes next to aluminium and iron in the order of abundance in the earth.

Calcium is best prepared by decomposing the iodide by metallic sodium: —

$$CaI_2 + 2\,Na = 2\,NaI + Ca.$$

Calcium is a silvery-white metal, which decomposes water slowly at ordinary temperatures.

Calcium Hydride, CaH_2, is formed by the action of hydrogen on the hot metal. Strontium and barium form similar compounds.

Calcium Oxide or Lime, CaO. — Calcium combines with oxygen, forming the oxide, CaO. The oxide is most conveniently prepared by heating the carbonate: —

$$CaCO_3 = CO_2 + CaO.$$

Calcium oxide is a white, amorphous powder, which is extensively used in a number of chemical operations.

Calcium oxide does not melt until a very high temperature is reached (about 3000°). It is, therefore, used in constructing the *Drummond light*. When the flame from the oxyhydrogen blowpipe is allowed to play upon a cylinder of lime, it becomes highly heated and at this high temperature gives out an enormous amount of light.

Calcium Hydroxide or Slaked Lime, $Ca(OH)_2$. — When lime or calcium oxide is thrown into water, a large amount of heat is evolved and calcium hydroxide is formed: —

$$CaO + H_2O = Ca(OH)_2.$$

This process is known as *slaking*.

Calcium hydroxide is a white powder, soluble in water only to the extent of 0.002 part in one part of water. This solution is known as *lime-water*. A mechanical suspension of the finely divided calcium hydroxide in water is known as *milk of lime*.

Calcium hydroxide is a strongly dissociated compound. It dissociates thus: —

$$Ca(OH)_2 = \overset{++}{Ca},\ \overset{-}{OH},\ \overset{-}{OH}.$$

Its solution contains a large number of hydroxyl ions, and it is, therefore, a very strong base. When a clear solution of calcium hydroxide is allowed to stand exposed to the air for a short time, it takes up carbon dioxide from the air, forming flakes of the insoluble calcium carbonate: —

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

When lime is exposed to the air, the same reaction takes place to some extent. Calcium oxide takes up moisture from the air, forming the hydroxide, and this combines in part with carbon dioxide, forming the carbonate. The white powder formed when lime is exposed to the air, known as *air-slaked lime*, is, then, a mixture of calcium oxide and calcium carbonate. Lime mixed with caustic soda is known as *soda-lime*.

Calcium Chloride, $CaCl_2$, $6\,H_2O$. — Calcium chloride, $CaCl_2$, $6\,H_2O$, is very soluble in water, producing, when dissolved, a considerable lowering of temperature. By mixing this salt in the proper proportions with finely powdered ice a temperature as low as $-30°$ to $-35°$ can be produced. The salt is most readily prepared by dissolving marble in hydrochloric acid, and evaporating the solution to crystallization.

On account of its attraction for water anhydrous calcium chloride is frequently used as a drying agent, especially for gases. These are passed slowly through tubes filled loosely with calcium chloride, and most of the water is removed from the gases and absorbed by the chloride.

Calcium Hypochlorite, Bleaching-powder, $Ca(OCl)_2$. — When chlorine is conducted into lime, it is absorbed by the lime. The reaction which takes place may be represented thus: —

$$2\,Ca(OH)_2 + 2\,Cl_2 = CaCl_2 + Ca(OCl)_2 + 2\,H_2O, \qquad (1)$$

giving a mixture of calcium chloride and hypochlorite; or it may be represented thus: —

$$2\,Ca(OH)_2 + 2\,Cl_2 = 2\,Ca\begin{matrix}<^{OCl}_{Cl}\end{matrix} + 2\,H_2O, \qquad (2)$$

forming one compound, which is half chloride and half hypochlorite.

It is difficult to decide between these two possibilities. The fact that bleaching-powder is not deliquescent, while calcium chloride is strongly deliquescent, would indicate that there is no calcium chloride in bleaching-powder. When treated with an acid bleaching-powder gives up all of its chlorine: —

$$Ca\begin{matrix}<^{OCl}_{Cl}\end{matrix} + 2\,HCl = CaCl_2 + H_2O + Cl_2.$$

Calcium Sulphate, $CaSO_4$. — The sulphate of calcium containing two molecules of water of crystallization, and known as *gypsum* — $CaSO_4 . 2 H_2O$ — occurs abundantly in nature. It dissolves in water to some extent, 2 parts in 1000, and is frequently found in solution. It also occurs in the solid form in many localities.

Gypsum is useful chiefly on account of the transformations which take place when its water is removed by heat, and the anhydrous salt is brought again into contact with water. When gypsum is heated to 107° it loses a part of its water: —

$$2 CaSO_4 . 2 H_2O = 2 CaSO_4 . H_2O + 3 H_2O.$$

Gypsum which is thus partially dehydrated is a flowery powder, and is known as *plaster of paris*. When brought in contact with water, plaster of paris takes it up again and forms gypsum. The mass, however, is now finely divided, and hardens after a few minutes. It is used extensively for making mouldings and casts of objects, especially of marble statuary.

If the temperature to which the gypsum is heated is at all high (200°), it loses all of its water. When the completely dehydrated product is brought in contact with water, it combines with the water very slowly, and is useless as far as making mouldings is concerned. Such gypsum is known as *hard-burned* or *dead-burned* gypsum.

Calcium Carbide, CaC_2. — Calcium carbide has come into very great importance recently on account of its method of preparation, and because when brought into the presence of water it readily yields the illuminant acetylene.

The carbide of calcium is prepared by heating a mixture of finely divided carbon and lime in an electric furnace: —

$$3 C + CaO = CO + CaC_2.$$

Its commercial value depends entirely upon the fact that it decomposes with water, giving *acetylene* gas: —

$$CaC_2 + H_2O = CaO + C_2H_2.$$

Acetylene gas has recently come into great prominence as an illuminant. This is due to the ease with which it can be made from calcium carbide. Water is admitted slowly to the carbide when the acetylene is desired, and a slow or rapid current of the gas generated at will.

Calcium Carbonate, $CaCO_3$. — The most abundant and important compound of calcium which occurs in nature is the carbonate. *Calcite* is well-crystallized calcium carbonate. It occurs in beautifully transparent, crystalline masses in Iceland, and is known as *Iceland spar*. Another crystalline variety of calcium carbonate is *aragonite*.

Calcium carbonate occurs in great abundance in less beautifully crystallized condition. *Marble* is a crystallized form of calcium carbonate. *Limestone* is also calcium carbonate, and is usually crystalline, but the crystals are generally smaller than in marble and are contaminated with various impurities. *Chalk* is a very fine-grained variety of calcium carbonate, formed chiefly of the shells of microscopic organisms. Indeed, calcium carbonate is frequently of organic origin, consisting of shells of animals which have been more or less metamorphosed by the geological processes to which they have been subjected.

Calcium carbonate can be readily formed in the laboratory by treating a soluble calcium salt with a soluble carbonate: —

$$CaCl_2 + Na_2CO_3 = 2\,NaCl + CaCO_3.$$

When calcium carbonate is heated, it undergoes decomposition into lime and carbon dioxide, as we saw when we were studying lime: —

$$CaCO_3 = CaO + CO_2.$$

Primary or Acid Calcium Carbonate, $Ca(HCO_3)_2$, is formed when the normal carbonate is dissolved in water containing carbon dioxide: —

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

Into water containing normal calcium carbonate in suspension conduct a current of carbon dioxide, and the calcium carbonate will pass into solution as the acid carbonate. The acid carbonate cannot, however, be isolated. Indeed, when its solution is boiled, the acid carbonate is decomposed into the normal carbonate and carbon dioxide is given off: —

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

When a solution of the acid carbonate is evaporated at ordinary temperatures, the normal carbonate is deposited. This is the way in which the *stalagma* in caverns are formed. The waters containing acid calcium carbonate in solution percolate through the roof of a cavern, and, evaporating, deposit calcium carbonate on the ceiling. This continues, the solution of the acid carbonate trickling over the outside of the deposit already formed, until frequently very beautiful hanging columns result. Such formations suspended from the ceiling or sides of a cavern are called *stalactites*. The solution of the acid carbonate frequently drops off of the stalactite, since the rate of evaporation in a closed space beneath the surface of the earth must be very slow. Where it drops on the floor of the cavern it evaporates and deposits the carbonate, and we frequently find columns and pillars of calcium carbonate growing upwards from the floor of caverns. Such growths are known as *stalagmites*.

Natural waters frequently contain carbon dioxide in considerable quantity. This is produced by decomposing vegetable matter in the soil through which they percolate, and is also taken from the atmospheric air. Consequently, many natural waters contain calcium carbonate in solution. Such are known as *hard waters*.

Phosphates of Calcium. — The three calcium salts of phosphoric acid are all known. They are the *tricalcium phosphate* or *normal* salt, $Ca_3(PO_4)_2$, the *secondary* salt, $CaHPO_4$, and the *primary* salt, $Ca(H_2PO_4)_2$.

Tricalcium phosphate, $Ca_3(PO_4)_2$, is found in large quantity in the bones of animals, and is therefore very important in

connection with animal life. When bones are heated to a high temperature in contact with the air, the organic matter is destroyed, and the calcium phosphate and other mineral matter in the bones remain behind in the *bone-ash.*

The normal calcium phosphate also occurs in nature as *phosphorite,* and in combination with calcium chloride or fluoride as *apatite.*

The phosphoric ions — *tertiary, secondary,* and *primary,* $\overset{\equiv}{PO_4}$, $H\overset{=}{P}O_4$, or $H_2\overset{-}{P}O_4$ — are of fundamental importance for the growth, and especially for the seeding, of plants. Among these are the very valuable cereals wheat and corn. These plants gradually remove the phosphoric acid ion from the soil, and the latter would soon become impoverished in this substance were it not supplied to the soil artificially. The most important constituent of commercial fertilizer is phosphoric acid ions.

Secondary calcium phosphate, $CaHPO_4$, is formed by the action of a soluble calcium salt on disodium phosphate in the presence of a little acid.

If a little acetic acid is added to the solution of disodium phosphate and calcium chloride then introduced, the tricalcium phosphate is formed at once: —

$$3\ CaCl_2 + 2\ Na_2HPO_4 + (CH_3COOH)$$
$$= Ca_3(PO_4)_2 + 4\ NaCl + 2\ HCl + (CH_3COOH).$$

If tricalcium phosphate is treated with a strong acid, *i.e.* with a concentrated solution of hydrogen ions in the proper proportions, the *primary calcium phosphate* is formed: —

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 = 2\ CaSO_4 + Ca(H_2PO_4)_2.$$

This is the commercial *superphosphate.*

In preparing *commercial fertilizer* the tertiary calcium phosphate is the starting-point in obtaining phosphoric acid ions.

The tricalcium phosphate in ground bone, or in finely ground phosphate rock, is treated with sulphuric acid and converted into phosphates which are somewhat soluble in water. This

is known as *soluble or available* phosphoric acid, while the phosphoric acid in the form of tricalcium phosphate is known as *insoluble* phosphoric acid.

Calcium Silicate, $CaSiO_3$.—The silicate of calcium occurs in nature in such well-known minerals as *mica* and *garnet*. Its chief importance is in connection with the manufacture of *glass*. Glass is, in general, an amorphous mixture of the silicate of calcium with the silicates of the alkalies. There are a number of varieties of glass, and a few of these will be reconsidered.

Glass is made by fusing together sand, calcium carbonate, and the carbonate of the alkali desired. If sodium carbonate is used, we have soda glass; if potassium carbonate is employed, potash glass, etc.

Soda glass is prepared by fusing together sodium carbonate, calcium carbonate, and silicon dioxide. Soda glass is readily fusible, and is easily attacked by chemical reagents such as boiling alkalies. It is blown into cylinders, which are then opened and flattened, and cut into ordinary window panes. This is known as *soft glass*, because it is easily worked in the blast-lamp, and has applications in the chemical laboratory, although, on account of its solubility, it is not well adapted for bottles for holding chemical reagents.

Bohemian or potassium glass is a potassium calcium silicate. It is much harder than the soda glass, fuses at a much higher temperature, and is much more resistant to chemical reagents. It is, therefore, valuable to the chemist, and is extensively employed in the manufacture of apparatus which is to be heated to a high temperature, such as combustion-tubing and the like.

Flint-glass consists of potassium and lead silicates, the lead taking the place of calcium in ordinary soda or potassium glass. It has such a high refractive power that it is used in making optical lenses.

The *colored glasses* are prepared by adding to the fused silicates, oxides of certain metals which give the desired color to the glass. *Yellow glasses* owe their color to uranium or antimony; *blue glasses* to cobalt or manganese; *red glasses* to copper,

iron, or sometimes gold; *green glasses* to chromium or copper, and so on. Glasses of almost every shade of color have been prepared by using different coloring constituents or mixtures of these constituents.

Most of the glass objects with which we are ordinarily familiar are *blown*. A large ball of molten glass is taken on the end of a hollow metal tube, through which the breath can be blown. The tube is then moved rapidly backwards and forwards through the air beneath the glass-blower, who drives air through the tube at the desired rate and time. The glass usually takes the form of a hollow cylinder, which is blown out to the desired thickness. This is cracked, flattened, and cut into the desired size. In this way flat panes of glass are made. Bottles are blown into moulds, and other glass objects of definite shape are either blown into moulds or moulded. Such objects must be *annealed*.

The properties of the glass is largely conditioned by the way in which it is annealed. If glass is cooled with moderate rapidity, it has the properties which we ordinarily associate with it. If cooled very rapidly, however, it has very different properties. It is under a considerable strain, and when the surface is fractured in any way, the glass flies in pieces almost with explosive violence.

The *Prince Rupert drops*, made by dropping molten glass into water, are examples of this condition.

On the other hand, when glass is cooled very slowly, as by introducing it when hot into hot oil, or by placing it in an oven which is cooled slowly, it is much less easily broken than ordinary glass. It acquires considerable elasticity, and can be struck a fairly hard blow without injury.

STRONTIUM (At. Wt. = 87.68)

The element strontium resembles calcium very closely in its properties, and in the properties of its compounds. It will, therefore, be treated very briefly, certain differences between the two being pointed out.

Occurrence, Preparation, and Properties of Strontium. — Stontium occurs in nature chiefly in the form of two salts which are well-known minerals. These are strontium carbonate or *strontianite*, and strontium sulphate or *celestite*.

The element is prepared most conveniently by electrolyzing the fused chloride.

Strontium resembles calcium in its appearance and properties.

Salts of Strontium. — Strontium forms the bivalent ion $\overset{++}{Sr}$, which is strictly analogous to the calcium ion $\overset{++}{Ca}$. It combines with two hydroxyl ions, forming *strontium hydroxide*, $Sr(OH)_2$, whose aqueous solution is strongly basic. This substance is more soluble in water than calcium hydroxide, and crystallizes from the aqueous solution with eight molecules of water: $Sr(OH)_2 \cdot 8\,H_2O$. *Strontium nitrate*, $Sr(NO_3)_2$, like strontium salts in general, gives a beautiful red color to a colorless flame. It is used, because of this property, to produce red light in fireworks and other pyrotechnic displays.

The strontium ion combines with the anions of acids, forming in general the same insoluble compounds as calcium. Certain differences in the degree of solubility, however, manifest themselves. Strontium combines with the ion $\overset{=}{SO_4}$, forming *strontium sulphate*, $SrSO_4$. This salt occurs in nature as *celestite*, and since it is only slightly soluble in water, is formed when a soluble sulphate is added to a soluble strontium salt: —

$$Na_2SO_4 + SrCl_2 = 2\,NaCl + SrSO_4.$$

Strontium sulphate is much less soluble in water than calcium sulphate, and is practically insoluble in a mixture of water and alcohol.

BARIUM (At. Wt. = 137.4)

An element closely allied to calcium and strontium is barium. This element occurs chiefly as the sulphate, $BaSO_4$, which is known as *barite* or *heavy spar*; and as the carbonate, $BaCO_3$, known as *witherite*.

Barium, like strontium and calcium, is prepared by electrolyzing the fused chloride. The metal barium is white, takes up oxygen from the air, and decomposes water with evolution of hydrogen.

Oxides of Barium. — Barium forms two oxides — the normal oxide, BaO, and the dioxide, BaO_2. *Barium oxide*, BaO, is formed by heating the nitrate: —

$$2\,Ba(NO_3)_2 = 2\,BaO + 4\,NO_2 + O_2.$$

Barium dioxide, BaO_2, is formed by heating the oxide to 500° in a current of air or oxygen: —

$$2\,BaO + O_2 = 2\,BaO_2.$$

Barium dioxide is an excellent "carrier of oxygen," since at a somewhat higher temperature it gives up its excess of oxygen and forms barium oxide again: —

$$2\,BaO_2 = 2\,BaO + O_2.$$

We have already become familiar with this substance in connection with the preparation of hydrogen dioxide. When it is treated with an acid, the following reaction takes place: —

$$BaO_2 + 2\,HCl = BaCl_2 + H_2O_2.$$

Barium Hydroxide, $Ba(OH)_2$. — The hydroxide of barium is formed when the oxide is dissolved in water: —

$$BaO + H_2O = Ba(OH)_2.$$

Barium oxide is much more soluble in water than strontium oxide, which in turn is more soluble than calcium oxide.

Barium Sulphate, $BaSO_4$. — The sulphate of barium, or *heavy spar*, occurs in nature as stated above. It is really formed whenever a soluble sulphate is added to a soluble barium salt: —

$$Ba(NO_3)_2 + K_2SO_4 = 2\,KNO_3 + BaSO_4.$$

It is the most insoluble sulphate known, and is, therefore, the form in which sulphuric acid is precipitated and weighed in quantitative determinations of this acid.

One decomposition of barium sulphate is of more than ordinary interest. *When the sulphate is boiled with a solution of sodium carbonate, it is transformed in part into barium carbonate:* —

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$

This transformation is at first only partial. If the solution of sodium carbonate and sodium sulphate is poured off after a time, and a new solution of sodium carbonate added, the decomposition of the barium sulphate into carbonate will proceed farther. By repeating this for a few times, practically all of the barium sulphate can be transformed into carbonate. This is one of the very best examples of the *effect of mass on chemical activity.* By renewing the solution of sodium carbonate, *i.e. by increasing its mass,* and by pouring off the solution of sodium sulphate formed, *i.e. by decreasing its mass,* the transformation in the sense of the above equation can be made practically complete.

The Law of Mass Action. — We have seen a number of examples of the effect of mass on chemical activity. The effect has been studied exhaustively in a great many cases, and the action of mass so well worked out that it can be formulated in a simple algebraic expression. If we represent the quantities of two substances in solution which are reacting chemically by p and q, and the quantities of the two substances formed by p_1 and q_1, the following relation obtains: —

$$pqk = p_1q_1k_1,$$

in which k and k_1 are two constants whose values depend upon the nature of the substances in question.

This generalization, whose significance cannot at this stage in the study of chemistry be fully appreciated, is of fundamental importance in dealing with the *nature* of chemical reactions and with the *velocities* with which they take place.

Relations between Calcium, Strontium, and Barium. — The three alkaline earth metals resemble one another closely in

their chemical properties. Certain differences, however, manifest themselves. The different solubilities of the salts of these elements with a given acid are very important, especially in connection with the separation of these elements from one another.

Take the hydroxides of the three elements: Calcium hydroxide is the least soluble; strontium hydroxide is more soluble than calcium; while barium hydroxide is still more soluble than strontium hydroxide.

When we turn to the sulphates, we find exactly the opposite relations. Barium sulphate is the most insoluble of the three; then comes strontium sulphate, and finally calcium sulphate.

All three of these elements form insoluble carbonates, while barium alone forms an insoluble chromate.

These differences in solubility are made use of to detect the alkaline earths when in solution in the presence of one another.

The Spectroscopic Study of the Alkalies and Alkaline Earths. — When white light is passed through a glass prism, it is bent out of its course, or refracted, as we say. White light is not homogeneous, but is composed of several different colors. Light of one color is bent to a different extent from light of another color. This can be seen by allowing white light to fall on a prism of glass, and placing the eye on the opposite side of the prism. We would see a number of colors arranged in a definite order from red through yellow to green and blue. These are known as the *prismatic colors.*

An instrument has been devised for breaking up light into its several colors. This is known as the *spectroscope.* It consists essentially of a prism, a tube containing at one end a narrow slit through which the incident light enters, and another tube through which the refracted light is seen.

If light of a definite color is placed in front of the spectroscope, it will appear in the instrument as a bright line or bright lines. When sodium light is viewed through a spectroscope, a bright yellow line will appear.

The spectroscope should also be provided with a scale, so

that the exact position of any line can be determined. The line produced by an element has a *perfectly definite and fixed position, and can be used to determine whether the element is present.* This principle is utilized in *spectroscopic analysis.* Where several elements are present, all of which give colored flames, it is impossible by examining the flame with the eye alone to tell which is present. Knowing the exact position in the spectroscope of the line (or lines) produced by the different elements, it is only necessary to throw the light from a flame containing any number of elements upon a spectroscope, in order to read off at once what elements are present.

The spectroscope has been of the greatest use to the chemist in identifying substances, in determining whether they were pure, and in the discovery of new elements.

EXPERIMENTS WITH CALCIUM, STRONTIUM, AND BARIUM

Experiment 150. Lime formed by Heating Calcium Carbonate. — (A small piece of marble; a piece of charcoal; blowpipe.)

Heat a piece of marble upon a piece of charcoal with the tip of the flame of the blowpipe. After heating the marble for several minutes throw it into water. Test the reaction of the water with red litmus paper. (See page 240.)

Experiment 151. Slaking of Lime; Properties of Calcium Hydroxide. — (Freshly burned lime; soluble salts of the same heavy metals as in Experiment 143.)

Treat 50 grams of freshly burned lime in a porcelain dish with a little water. The water is taken up and a large amount of heat is evolved. The lime crumbles and falls to pieces, yielding a fine powder. This is *slaked lime* or *calcium hydroxide.* Treat a part of this powder with a litre or two of water. Allow the solution to settle and decant the clear liquid. This is *lime-water*, or calcium hydroxide, in solution.

Calcium hydroxide has properties closely allied to those of potassium hydroxide. Treat solutions of salts of the heavy metals with lime-water; the hydroxides of the heavy metals are thrown down. Compare the results with those obtained in Experiment 143. (See page 240.)

Experiment 152. Preparation and Properties of Calcium Chloride. — (Marble; hydrochloric acid; thermometer.)

Dissolve marble in hydrochloric acid, using an excess of marble. Evaporate the solution and calcium chloride will crystallize out. Mix the powdered crystals of calcium chloride with one-third their volume of sodium chloride. Plunge a thermometer into the mixture. What evidence have you that there is a marked lowering of temperature? (See page 240.)

Experiment 153. Gypsum; Plaster of Paris. — (Gypsum.)

Heat a little gypsum to 140° for a number of hours. It is partly dehydrated, and forms a flowery powder — plaster of paris. Add a little water to plaster of paris. It forms a pasty mass, which rapidly hardens and can be used for moulding objects.

Heat a little gypsum to 200° for an hour or two. Add water. Does it behave like plaster of paris? What is the difference? (See page 242.)

Experiment 154. Calcium Carbide. — (Calcium carbide.)

Introduce a small piece of calcium carbide into a test-tube and drop water slowly upon it. Smell the odor of the escaping gas. Does it burn? What remains in the test-tube? Add a little of the solution to solutions of salts of the heavy metals. What are precipitated? (See page 242.)

Experiment 155. Calcium Carbonate and Acid Calcium Carbonate. — (Lime-water; carbon dioxide generator.)

Pass carbon dioxide into lime-water. Insoluble calcium carbonate will be precipitated. Write the equation?

Continue to pass carbon dioxide into water containing calcium carbonate in suspension. The calcium carbonate will pass into solution again. Write equation and explain the fact?

Boil the clear solution; calcium carbonate will be precipitated again. Explain? Write equation?

Pass carbon dioxide again through the solution containing calcium carbonate in suspension. It will redissolve? (See page 243.)

Experiment 156. Flame Reaction of Calcium. — (Calcium compound; platinum wire.)

Dip a clean platinum wire into a calcium compound and insert the wire into the colorless flame of a bunsen burner. Note the orange-red color imparted to the flame by the calcium compound. This flame is characteristic of calcium.

Experiment 157. Flame Reaction of Strontium. — (Strontium compound; platinum wire.)

Introduce a strontium compound on a clean platinum wire into a bunsen flame. Note the deep red color imparted to the flame. This flame reaction is characteristic of strontium.

Experiment 158. Properties of Barium Hydroxide. — (Baryta water; soluble carbonates; soluble salts of the heavy metals.)

Treat a number of soluble carbonates with baryta water. White barium carbonate is precipitated. Add acid to barium carbonate. What takes place?

Treat solutions of salts of the heavy metals (lead nitrate; zinc chloride; cadmium chloride; aluminium chloride; chromium chloride, etc.) with baryta water. What is formed?

Barium hydroxide, like strontium hydroxide, behaves like calcium hydroxide. They all resemble chemically the hydroxides of the alkalies. (See page 249.)

Experiment 159. Barium Sulphate decomposed by Sodium Carbonate. — (Barium chloride; sodium sulphate; sodium carbonate.)

To a solution of barium chloride add a solution of sodium sulphate. Insoluble barium sulphate is precipitated. Filter this off and wash thoroughly with hot water.

Transfer the barium sulphate to a small beaker and pour over it a solution of sodium carbonate. Boil for ten or fifteen minutes. Then filter off the solution and test for sulphuric acid in the filtrate, by adding barium chloride and hydrochloric acid. Hydrochloric acid is added to prevent barium carbonate from being precipitated. Explain?

Sulphuric anions will be found in the filtrate due to the formation of sodium sulphate, which is soluble. (See page 250.)

Experiment 160. Flame Reaction of Barium. — (Barium compound; platinum wire.)

Introduce a barium compound on a clean platinum wire into a colorless bunsen flame. A bright green color will be imparted to the flame. This is the characteristic flame reaction of barium.

Experiment 161. Spectroscopic Examination of the Alkalies and Alkaline Earths. — (Sodium salt; potassium salt; calcium salt; strontium salt; barium salt; fine pieces of platinum wire; spectroscope.)

Clean the platinum wires by dipping them into hydrochloric acid, and plunge one into each of the above salts.

Place these wires, one at a time, in the colorless flame in front of the spectroscope. Observe the bright lines which flash out in each case. Carefully note the color and position of the lines in the spectroscope in each case. The exact position of the lines is characteristic of the element in question. (See page 251.)

PROBLEMS

1. What weight of lime and of carbon dioxide can be obtained from 1 kilogram of marble? How much bleaching-powder from the above amount of lime?
2. Weight of acetylene obtainable from the calcium carbide which can be formed from 1 gram of carbon?
3. Amount of strontium nitrate which could be formed from 100 grams of strontium hydroxide? Percentage of strontium in each substance?
4. Weight of the barium sulphate which would be precipitated when sulphuric acid is added to a solution containing 0.75 gram of barium nitrate?

CHAPTER XX

THE MAGNESIUM GROUP

GLUCINUM, MAGNESIUM, ZINC, CADMIUM, MERCURY

GLUCINUM (At. Wt. = 9.1)

The first two members of this group, glucinum and magnesium, correspond rather closely in their properties to the elements of the calcium group. The first of these elements, glucinum or beryllium, is comparatively rare. It occurs chiefly in the mineral *beryl*, which is a silicate of aluminium and beryllium.

MAGNESIUM (At. Wt. = 24.36)

The second member of the series in the order of increasing atomic weights, but the first member in the order of importance, and the one from which the series takes its name, is magnesium. Magnesium occurs in nature in the form of several salts. Magnesium carbonate, *magnesite*, $MgCO_3$, is fairly widely distributed, while the double carbonate of magnesium and calcium, *dolomite*, forms whole mountain ranges. Magnesium also occurs as the sulphate, $MgSO_4 . H_2O$, — *kieserite*.

Carnallite, — the double chloride of potassium and magnesium — $KMgCl_3 . 6\ H_2O$, is also found in large quantities in certain salt deposits. The double silicates of magnesium and other metals constitute some of the best-known minerals, such as *hornblende*, *serpentine*, *talc*, *asbestos*, etc.

Magnesium is prepared by electrolyzing fused, anhydrous carnallite. When heated it takes fire and burns with a brilliant white light, which, on account of its richness in light of short wave-lengths, is frequently used for illuminating purposes in photography.

Magnesium Oxide, MgO, and Magnesium Hydroxide, $Mg(OH)_2$. — Magnesium oxide, or *magnesia*, is formed when magnesium is burned in the air, or when the carbonate or hydroxide of magnesium is heated. Magnesia melts only at enormously high temperatures. It is, therefore, used to line vessels which are subjected to high temperatures.

Magnesium oxide dissolves in water to only a slight extent, forming, however, magnesium hydroxide.

Magnesium Chloride, $MgCl_2 . 6\ H_2O$. — Magnesium chloride, like the chlorides of calcium and strontium, contains six molecules of water of crystallization. It occurs in nature in combination with potassium chloride as *carnallite*, and can readily be prepared by dissolving magnesium carbonate or oxide in hydrochloric acid.

Magnesium Sulphate, $MgSO_4 . 7\ H_2O$. — Magnesium sulphate containing one molecule of water, occurs in nature as the mineral *kieserite*, $MgSO_4 . H_2O$. The ordinary salt, known as *Epsom salt* since it is contained in the Epsom springs, contains seven molecules of water, $MgSO_4 . 7\ H_2O$.

Magnesium sulphate is used in medicine as a purgative.

Phosphates of Magnesium. — Magnesium forms the *primary* $Mg(H_2PO_4)_2$; the *secondary*, $MgHPO_4$; and the *tertiary*, or *normal*, phosphate, $Mg_3(PO_4)_2$. These resemble the phosphates of calcium so closely that a detailed discussion is unnecessary. One phosphate of magnesium, however, is of special interest. This is the *ammonium magnesium phosphate* already mentioned — $NH_4MgPO_4 . 6\ H_2O$.

When heated it decomposes as follows: —

$$2\ NH_4MgPO_4 = 2\ NH_3 + H_2O + Mg_2P_2O_7,$$

yielding *magnesium pyrophosphate*, which is a very stable substance and of constant composition. It is, therefore, an excellent form in which to weigh either phosphoric acid or magnesium.

Magnesium Nitride, Mg_3N_2, is formed by the direct action of nitrogen on red-hot magnesium. Calcium and barium also form nitrides quite readily.

ZINC (At. Wt. = 65.4).

An element closely allied to magnesium in many of its properties, but differing from it markedly in others, is zinc. This well-known element occurs in nature in abundance in a number of compounds. *Zinc blende*, which is the sulphide, ZnS, is one of the most common. It also occurs as the carbonate, $ZnCO_3$, *smithsonite*, and the silicate, Zn_2SiO_4, *calamine*.

Zinc is prepared by reducing with carbon the oxide, which is usually obtained by roasting the sulphide in the air: —

$$ZnO + C = CO + Zn.$$

The metal boils at 950°, and is, therefore, easily distilled off when once set free. It condenses in the form of a fine powder or dust, which is known as *zinc dust*. The metal can be melted and cast into sticks, or poured into water while molten and produces *granulated zinc*.

Zinc is used for covering objects which if exposed to air or water would rust. Iron objects thus protected are known as *galvanized*. Iron objects are galvanized by dipping them into molten zinc. Zinc is also extensively used in constructing primary cells. The chief uses of zinc, however, are as alloys with other metals. The best known of these is *brass*, an alloy with copper. When nickel is added, we have the alloy of zinc, copper, and nickel, known as *German silver*.

Zinc readily combines with mercury when the clean surface of the metal is brought in contact with the mercury, forming *zinc amalgam*.

Zinc Oxide, ZnO, and Hydroxide, $Zn(OH)_2$. — Zinc oxide is formed when zinc burns in the air. It is known from its general appearance as *philosopher's wool*. It is prepared more conveniently by heating basic zinc carbonate. This loses carbon dioxide and water, and zinc oxide remains behind. Zinc oxide is used as a pigment under the name of *zinc white*.

Zinc hydroxide, $Zn(OH)_2$, is formed when a soluble zinc salt is treated with a small amount of an alkaline hydroxide: —

$$ZnCl_2 + 2\,KOH = 2\,KCl + Zn(OH)_2.$$

Zinc hydroxide is a white, flocculent precipitate, which dissolves readily in acids forming the corresponding salts. It is therefore *basic with respect to acids*, and as it dissolves, must dissociate into zinc and hydroxyl ions, thus: —

$$Zn(OH)_2 = \overset{++}{Zn},\ \overset{-}{OH},\ \overset{-}{OH}. \qquad (1)$$

Zinc hydroxide also dissolves in strong alkalies, forming salts with these, in which the hydroxide plays the rôle of an acid. If zinc hydroxide is treated with potassium hydroxide in excess, the white precipitate dissolves, forming *potassium zincate*: —

$$Zn(OH)_2 + 2\ KOH = K_2ZnO_2 + 2\ H_2O.$$

The zinc hydroxide, in the presence of a strong base, acts then as an acid, and must dissociate so as to yield hydrogen ions: —

$$Zn(OH)_2 = \overset{+}{H},\ \overset{+}{H},\ \overset{=}{ZnO_2}. \qquad (2)$$

The kinds of ions into which certain compounds dissociate is conditioned, then, by the nature of the substance into whose presence they are brought. Thus, zinc hydroxide in the presence of hydrogen ions, dissociates in the sense of equation (1); in the presence of hydroxl ions, in the sense of equation (2).

Zinc Chloride, $ZnCl_2 . H_2O$. — The chloride of zinc is readily formed by dissolving zinc in hydrochloric acid and evaporating the solution to crystallization. When the salt is heated to remove the water it loses hydrochloric acid, and a basic chloride remains behind.

To obtain pure, anhydrous, zinc chloride, the salt with water of crystallization must be heated in an atmosphere of dry hydrochloric acid gas.

Zinc Sulphide, ZnS. — The sulphide of zinc has been referred to as occurring in nature as zinc blende, and as being one of the most important ores of zinc. It is formed as a white precipitate whenever hydrogen sulphide is conducted into a dilute solution of a soluble zinc salt: —

$$ZnCl_2 + H_2S = 2\ HCl + ZnS.$$

The sulphide of zinc is soluble to some extent in strong acids, *i.e.* in the presence of hydrogen ions. In a reaction like the above where a strong acid is liberated, the precipitation of zinc sulphide is not complete unless the solution is very dilute, since a portion of it is dissolved in the hydrochloric acid formed as the result of the reaction.

If the solution of the zinc salt is treated with a solution of an alkaline sulphide, the zinc is completely precipitated, since no free acid is formed as the result of the reaction: —

$$ZnCl_2 + K_2S = 2\,KCl + ZnS.$$

Zinc Sulphate, $ZnSO_4 . 7\ H_2O$. — The sulphate of zinc is obtained when a bar of pure zinc is wrapped with a piece of platinum wire, dissolved in pure sulphuric acid, and the solution evaporated to crystallization. The salt is formed on a large scale by heating the sulphide in the presence of oxygen: —

$$ZnS + 2\,O_2 = ZnSO_4.$$

Like other sulphates containing a large number of molecules of water of crystallization, it retains one molecule to a much higher temperature than the remainder. When zinc sulphate is heated slightly above 100° it loses six molecules of water. The last molecule is retained until a considerably higher temperature is reached. On account of its color and composition the salt is known as *white vitriol.*

Zinc Carbonate, $ZnCO_3$, is an important ore of zinc. When heated it decomposes into the oxide and carbon dioxide: —

$$ZnCO_3 = ZnO + CO_2.$$

CADMIUM (At. Wt. = 112.35)

A comparatively rare element which is closely allied in its properties to zinc is cadmium. It usually occurs associated with zinc ores, either in the form of the oxide or sulphide. The oxide of cadmium, like that of zinc, is easily reduced by heated carbon: —

$$CdO + C = CO + Cd.$$

MERCURY (At. Wt. = 200.0)

Mercury occurs in nature in the elementary condition, but much more abundantly in the form of the sulphide, HgS, *cinnabar*. The chief localities are Almadem in Spain and California. Mercury is readily obtained by heating the sulphide in contact with the air. The metal distils over and is condensed, and the sulphur is oxidized to sulphur dioxide.

Properties of Mercury. — Mercury combines with oxygen only at elevated temperatures, but combines with the halogens at ordinary temperatures. Mercury forms a univalent mercurous ion, $\overset{+}{Hg}$, and a bivalent mercuric ion, $\overset{++}{Hg}$. Both of these ions combine with the anions of acids, forming salts. The former are known as *mercurous*, the latter as *mercuric*, salts.

Amalgams. — Many of the metals dissolve readily in mercury, forming amalgams, which are really solutions of the metals in mercury as a solvent. Such metals as magnesium, zinc, cadmium, silver, gold, the alkaline earths, the alkalies, and many others dissolve without serious difficulty in mercury.

The amalgams of sodium have already been referred to. The one containing one per cent of sodium is a liquid, while double the amount of sodium gives a solid solution in mercury.

The ammonium amalgam formed by bringing ammonium chloride in contact with sodium amalgam, has also been referred to (p. 79).

Mercurous (Hg_2O) and Mercuric (HgO) Oxides. — Mercurous oxide is formed when a mercurous salt is treated with an alkali: —

$$2\ HgCl + 2\ NaOH = 2\ NaCl + H_2O + Hg_2O.$$

By light, heat, or friction, it is decomposed into mercury and oxygen. It is a black powder and quite unstable.

Mercuric oxide is formed when mercury is heated for a long time in the air. It is also obtained as a *red* powder by heating the nitrate.

It is also formed by treating a mercuric salt with sodium hydroxide: —

$$HgCl_2 + 2\ NaOH = 2\ NaCl + H_2O + HgO.$$

Prepared in this way it is *yellow*, but becomes red on gentle heating.

Mercurous (HgCl) and Mercuric ($HgCl_2$) Chlorides. — Mercurous chloride is the familiar substance *calomel*. It is formed by heating a mercurous salt with a soluble chloride: —

$$Hg_2SO_4 + 2\ NaCl = Na_2SO_4 + 2\ HgCl.$$

Mercurous chloride is readily oxidized to the mercuric salt, which is quite poisonous.

Mercurous chloride is partly transformed into mercuric chloride by the action of light. When calomel is exposed for a considerable time to the action of light, it contains the very poisonous substance mercuric chloride, and should never be used as a medicine. Calomel which is to be used for such purposes should always be carefully protected from all agents which transform it into mercuric chloride. Mercuric chloride, or *corrosive sublimate*, is formed by subliming a mixture of sodium chloride and mercuric sulphate. The following reaction takes place: —

$$2\ NaCl + HgSO_4 = Na_2SO_4 + HgCl_2.$$

Mercuric chloride is a white, crystalline compound, readily soluble in water.

On account of its solubility it furnishes a convenient means of obtaining mercuric ions, $\overset{++}{Hg}$, which are very poisonous to most forms of life. *Mercuric chloride is, therefore, an excellent disinfectant*, and is extensively used in surgery for this purpose.

Mercuric Sulphide, HgS. — Only one compound of mercury with sulphur is known, and this is the one in which the mercury is bivalent. When hydrogen sulphide is brought into the

presence of a mercurous salt, a mixture of black mercuric sulphide and mercury is thrown down: —

$$2\ HgCl + H_2S = HgS + Hg + 2\ HCl.$$

When mercury and sulphur are rubbed together, the sulphide is formed. It is also formed by passing hydrogen sulphide for a time through a solution of a mercuric salt: —

$$HgCl_2 + H_2S = 2\ HCl + HgS.$$

Variable Valence. — We have studied a number of non-metals which showed different valence under different conditions. This is, however, the first metal which we have encountered in which two different valencies clearly manifest themselves. We have a well-defined mercurous ion, $\overset{+}{Hg}$, in which the mercury carries only one electrical charge. This forms, with the anions of acids, a class of salts which have definite properties. From these salts the mercurous mercury is precipitated by bases as the black mercurous oxide. Hydrochloric acid throws down insoluble mercurous chloride. Hydrogen sulphide precipitates a mixture of mercuric sulphide and mercury.

The mercuric ion, $\overset{++}{Hg}$, has its own characteristic properties, forming compounds also with the anions of acids. From these compounds it is precipitated by hydrogen sulphide as mercuric sulphide. The alkaline hydroxides precipitate mercuric oxide, while stannous chloride in excess throws down metallic mercury.

EXPERIMENTS WITH MAGNESIUM, ZINC, CADMIUM, AND MERCURY

Experiment 162. Magnesium burns in the Air. — (Magnesium ribbon.)

Ignite a piece of magnesium ribbon in a bunsen burner. It burns with an intense white light.

Collect the magnesium oxide formed, and dissolve in a large volume of water. Test the reaction of the solution with red

litmus. Add some of the solution to salts of the heavy metals. What are formed? (See page 257.)

Experiment 163. Formation of Magnesium Phosphate. — (Disodium phosphate; ammonia; any soluble magnesium salt.)

Add ammonia to a solution of disodium phosphate, and add some of this mixture to any soluble magnesium salt. White magnesium ammonium phosphate is precipitated. Prove that ammonia is given off when this compound is washed, dried, and heated. (See page 257.)

Experiment 164. Zinc Hydroxide Soluble in Sodium Hydroxide. — (Zinc chloride; sodium hydroxide.)

Introduce a few drops of zinc chloride into a test-tube, and add sodium hydroxide drop by drop. At first zinc hydroxide is thrown down as a white precipitate. The addition of more sodium hydroxide dissolves the precipitated zinc hydroxide, and the solution becomes clear again.

Zinc hydroxide thus differs from all the hydroxides thus far considered. Towards an acid it acts as a base, while towards a stronger base it acts as an acid. (See page 259.)

Experiment 165. Precipitation of Zinc Sulphide. — (Zinc chloride; ammonium sulphide.)

Add ammonium sulphide to a solution of zinc chloride. White zinc sulphide is precipitated. Filter off, wash with water, and treat with dilute hydrochloric acid. Does it dissolve? (See page 259.)

Experiment 166. Precipitation of Cadmium Sulphide. — (Cadmium chloride; hydrogen sulphide generator.)

Pass hydrogen sulphide through a cold, dilute solution of cadmium chloride. Yellow cadmium sulphide is precipitated. Filter off the precipitate, wash with hot water, and test its solubility in cold, dilute hydrochloric acid. (See page 260.)

Experiment 167. Formation of Amalgams. — (Zinc; cadmium; mercury.)

Bring a bar of zinc or of cadmium into contact with mercury. The metal dissolves in the mercury, which quickly changes its appearance, becoming a thick, viscous mass. (See page 260.)

Experiment 168. Precipitation of Mercury Sulphide. — (Mercuric chloride; hydrogen sulphide.)

Test the solubility of mercurous chloride.

Pass hydrogen sulphide into a solution of mercuric chloride. Black mercuric sulphide is precipitated. Test the solubility of the sulphide in dilute acids. (See page 262.)

PROBLEMS

1. Water of crystallization in 50 grams of magnesium sulphate. ($MgSO_4 . 7\ H_2O$.)
2. What is the percentage of magnesium in magnesium pyrophosphate?
3. How much zinc is present in 3 grams of sodium zincate? How much zinc blende is required to yield this amount of zinc?
4. Weight of the cadmium sulphide which would be formed by the cadmium in 1 gram of cadmium oxide?
5. What amount of mercurous and mercuric chlorides can be formed from the mercury in 5 grams of cinnabar?

CHAPTER XXI

ALUMINIUM (At. Wt. = 27.1)

Occurrence and Preparation. — Of the elements of this group only one occurs in any abundance, and this is aluminium. The remainder are rare substances.

Aluminium is a very important constituent of the crust of the earth. The oxide of aluminium, known as *corundum*, is abundant, and the precious stones *ruby* and *sapphire* are aluminium oxide colored by a small amount of other substances.

The double silicates of aluminium and the alkalies are among the most common minerals. *Mica* is a double silicate of aluminium and one of the alkalies, having the general composition $MAlSiO_4$, in which M is a univalent alkali. The more common *feldspars* are silicates of aluminium and one of the alkalies sodium or potassium. They have the general composition $MAlSi_3O_8$. *Kaolin* and *clay* are more or less pure hydrous silicates of aluminium, while *cryolite*, found in Greenland, is a double fluoride of sodium and aluminium, having the composition $3\,NaF\,.\,AlF_3$. This compound is of importance in connection with the preparation of the element.

Aluminium is prepared to-day by the electrolytic method. The compound electrolyzed is aluminium oxide. On account of the high fusing-point of aluminium oxide, a bath of cryolite is used and into the fused cryolite the aluminium oxide is introduced as desired. The cryolite is fused in iron crucibles, which are sometimes lined with carbon. This serves as the *cathode* or pole which receives the current from the solution, and upon this the metal separates; the oxygen set free combines with the *anode*, the pole from which the current enters

the solution, which consists of bars of carbon introduced into the fused cryolite. The mass is kept molten by the heat generated by the current. Since the introduction of the electrolytic method of preparing aluminium, this metal has become quite abundant and its price greatly reduced.

Properties of Aluminium. — Aluminium is a metal with remarkable properties. It is ductile and malleable and can be readily drawn into wire or hammered into thin foil. It is very light for a metal, having a specific gravity of only 2.7. It can, nevertheless, withstand considerable strain, but by no means as great as was supposed before it was prepared on a large scale. Its softness also detracts from its commercial value.

Chemically, aluminium is fairly resistant. In contact with moist air it becomes covered with a very thin layer of oxide, which protects the metal from further action. It dissolves readily in hydrochloric acid, while nitric and sulphuric acids act only at elevated temperatures.

Aluminium Oxide, Al_2O_3, and Hydroxide, $Al(OH)_3$. — The oxide of aluminium occurs in nature, as has already been mentioned. Its most common form is *corundum*. *Bauxite* also occurs in abundance. *Sapphire* is a blue variety used as a gem, while *ruby* is a red sapphire. A violet variety is known as *oriental amethyst*, and a yellow variety as *oriental topaz*.

Aluminium oxide is easily prepared by heating aluminium hydroxide: —

$$2\,Al(OH)_3 = Al_2O_3 + 3\,H_2O.$$

Aluminium hydroxide is readily prepared by treating a soluble aluminium salt with a base: —

$$AlCl_3 + 3\,NH_4OH = 3\,NH_4Cl + Al(OH)_3.$$

It is also formed when a soluble carbonate or sulphide is added to a soluble aluminium salt: —

$$2\,AlCl_3 + 3\,Na_2CO_3 + 3\,H_2O = 6\,NaCl + 3\,CO_2 + 2\,Al(OH)_3;$$
$$2\,AlCl_3 + 3\,(NH_4)_2S + 6\,H_2O = 6\,NH_4Cl + 3\,H_2S + 2\,Al(OH)_3.$$

Aluminium hydroxide is very slightly soluble in water, and is a very weak base. Since aluminium hydroxide is a triacid base, it must be capable of dissociating as follows: —

$$Al(OH)_3 = \overset{+++}{Al},\ \overset{-}{OH},\ \overset{-}{OH},\ \overset{-}{OH}.$$

Aluminium hydroxide also acts as an acid towards strong bases. When aluminium hydroxide is treated with a strong base like sodium hydroxide, the following reaction takes place: —

$$Al(OH)_3 + 3\,NaOH = 3\,H_2O + Na_3AlO_3.$$

This compound, known as *sodium aluminate*, is obviously the sodium salt of the acid H_3AlO_3. The question which arises here is, How can a compound which dissociates like aluminium hydroxide, yielding hydroxyl ions, have acid properties or yield hydrogen ions? When in contact with a base or hydroxyl ions, it dissociates as follows: —

$$Al(OH)_3 = \overset{+}{H},\ H_2\overset{-}{Al}O_3,$$
$$H_2\overset{-}{Al}O_3 = \overset{+}{H},\ H\overset{=}{Al}O_3,$$
$$H\overset{=}{Al}O_2 = \overset{+}{H},\ \overset{\equiv}{Al}O_3.$$

In a word, it dissociates as a tribasic acid. We have seen a similar phenomenon manifested by zinc, and other cases will appear later.

Cements. — The alkaline earths also form aluminates. Calcium forms the *normal aluminate* $Ca_3(AlO_3)_2$, and also the *meta-aluminate* $Ca(AlO_2)_2$. Since these salts harden in contact with water, they are used in connection with the preparation of *hydraulic cements*.

Aluminium Chloride, $AlCl_3 . 6\,H_2O$, is formed when aluminium hydroxide is treated with hydrochloric acid. From such a solution it can be obtained in crystalline form with six molecules of water, $AlCl_3 . 6\,H_2O$.

The *fluoride of aluminium*, as contained in *cryolite*, has already been referred to as occurring in Greenland, and as having the

composition Na_3AlF_6. It is obviously the sodium salt of the unknown hydrofluoraluminic acid, H_3AlF_6.

Aluminium Sulphate, $Al_2(SO_4)_3 . 18 H_2O$, is formed by treating aluminium hydroxide with sulphuric acid, and heating the mixture. On evaporating the solution, a salt of the above composition separates.

The Alums. — Aluminium sulphate combines with the sulphates of the alkalies to a remarkable extent, forming a class of double sulphates known as the alums. These have the general composition $MAl(SO_4)_2 . 12 H_2O$, in which M is an alkali atom. There are a large number of these substances; indeed, every alkali sulphate forms an alum with aluminium sulphate. The best known of these are potassium alum, $KAl(SO_4)_2 . 12 H_2O$, and ammonium alum, $NH_4Al(SO_4)_2 . 12 H_2O$. The alums all crystallize in the same system, as octahedra and cubes. This system, known as the *regular system*, has all three axes of equal length, and all make right angles with one another. The alums are all *isomorphous, i.e.* form crystals containing several of these substances. When a crystal of one alum is suspended in a solution of another alum, the second alum will be deposited upon it as upon one of its own crystals.

The term "alum" has been extended from the double sulphates of aluminium and the alkalies, to the double sulphates of allied elements and the alkalies. Thus we have a series of iron alums of the general composition $MFe(SO_4)_2 . 12 H_2O$, in which M is sodium, potassium, rubidium, cæsium, lithium, or ammonium. Similarly, we have a series of manganese alums, $MMn(SO_4)_2 . 12 H_2O$, and a series of chromium alums, $MCr(SO_4)_2 . 12 H_2O$. These all crystallize in the regular system, contain twelve molecules of water of crystallization, and are isomorphous with one another and with the corresponding aluminium compounds.

Aluminium Carbide, Al_4C_3. — Aluminium combines with carbon, forming the carbide, Al_4C_3. This was produced by Moissan, by heating aluminium in carbon boats in an electric

furnace; also in preparing aluminium by the electrolytic method, where the metal separates upon carbon electrodes.

When aluminium carbide is decomposed by water, we have: —

$$Al_4C_3 + 12\,H_2O = 3\,CH_4 + 4\,Al(OH)_3.$$

Aluminium hydroxide and *methane* are formed. Compare this with the decomposition of calcium carbide by water. (Page 242.)

Silicates of Aluminium. — These are very important substances. Aluminium forms salts not only with normal silicic acid, but also with the polysilicic acids. A comparatively pure form of aluminium silicate is known as *kaolin*. This substance has approximately the composition $Al_4(SiO_4)_3 \cdot 4\,H_2O$, being the aluminium salt of normal silicic acid.

Clay is an impure variety of aluminium silicate. This is formed as the result of the weathering of the rocks, and, consequently, many other substances are liable to be present in it. The different colors of clays are due to different impurities.

Marl is clay containing a large amount of calcium carbonate.

Aluminium silicate readily forms *double silicates* with the silicates of the alkalies, and these constitute some of the most important minerals, the *feldspars*. We have potassium feldspars, sodium feldspars, potassium sodium feldspars, etc. These have the general composition $MAlSi_3O_8$. The potassium feldspar is known as *orthoclase*, the sodium compound as *albite*.

Aluminium silicate forms double silicates with many other elements, especially with those of the calcium and iron group. Among the double silicates of aluminium are such minerals as the *garnets*, *mica*, *zeolites*, etc.

Applications of Aluminium Silicates. — When kaolin or clay is mixed with water, they form a thick viscous mass, which can be readily moulded or worked into any desired form. When this mass is dried and heated, it becomes very hard and then resists the action of water. It is from this material that ordinary *brick* or *fire-brick* is made.

Earthenware or *stoneware* is made from a variety of aluminium silicate somewhat purer than that employed in the manufacture of ordinary fire-brick. The objects are moulded from the purer varieties of clay or kaolin by mixing with water to the proper consistency. They are then "fired" or "baked" by heating to a high temperature. The resulting objects are, however, very porous, and would be comparatively useless in this form. They must be covered by a non-porous material — must be *glazed*. There are different methods of glazing such objects. A mixture of kaolin and feldspar melts at a comparatively low temperature, and this is sometimes applied to the surface of earthenware after it has been "burned," and the object then reheated.

Porcelain is made of pure aluminium silicate, or pure kaolin. This is mixed in definite proportions with feldspar to lower its melting-point, and also with quartz. The mixture is treated with water until the desired consistency is reached, and is then moulded into the desired form. It is then dried and "burned." The glaze consists of a mixture of feldspar, quartz, and lime. After applying the glaze, the vessel is heated again to a very high temperature. The many different varieties of porcelain owe their peculiar characteristics in part to the nature of the materials used, and in part to the way in which they are manipulated during manufacture.

Aluminium silicate is also an important constituent of many valuable *cements*.

In this same group belong the rare elements: *scandium*, *gallium*, *yttrium*, *indium*, *lanthanum*, and *thallium*.

EXPERIMENTS WITH ALUMINIUM

Experiment 169. Aluminium Hydroxide soluble in Sodium Hydroxide. — (Aluminium chloride or an aluminium alum; sodium hydroxide.)

Add sodium hydroxide, drop by drop, to a solution of aluminium chloride or an aluminium alum. Aluminium hydroxide

is precipitated as a white, gelatinous mass. Add more sodium hydroxide, and the aluminium hydroxide will dissolve again. Write the equations? What hydroxide already dealt with does this suggest? (See page 267.)

Experiment 170. Aluminium Hydroxide precipitated by a Soluble Carbonate or by Ammonium Sulphide. — Aluminium chloride or an aluminium alum; sodium carbonate; ammonium sulphide.)

Add sodium carbonate to a solution of an aluminium salt. A white precipitate resembling aluminium hydroxide is formed. Filter and wash with hot water. Add a little hydrochloric acid to the precipitate. It dissolves. Is carbon dioxide given off? It is aluminium hydroxide. Write the equations for the reactions?

A similar precipitate is thrown down by hydrogen sulphide, since aluminium sulphide is decomposed by water. Wash; add hydrochloric acid. The precipitates dissolve. Is hydrogen sulphide given off? The precipitate is aluminium hydroxide. Write equations? (See page 267.)

PROBLEMS

1. How much aluminium hydroxide can be prepared from the aluminium obtained from 2 grams of corundum? from 5 grams of cryolite?
2. Amount of aluminium chloride which could be formed from the aluminium in 8 grams of potassium alum?
3. Weight of hydrogen sulphide required to precipitate the aluminium in 3.4 grams of potassium aluminium sulphate? How much aluminium hydroxide would be thrown down?

CHAPTER XXII

IRON, COBALT, NICKEL

IRON (At. Wt. = 55.9)

We now come to a group which contains some of the most important elements technically, as well as some of the most interesting from the chemical standpoint. The first of these, and the one from which the group takes its name, is iron — the most important technically of all the elements.

Occurrence and Preparation. — Iron occurs very widely distributed in nature, but not in abundance in the free state. This is due especially to its action on water forming the hydroxide.

Iron occurs chiefly in the form of oxides and sulphides. It occurs in large quantities as *magnetite*, Fe_3O_4, as *hematite*, Fe_2O_3, and as *bog-iron ore*, *limonite*, and other hydroxides. Iron also occurs in large quantities as *pyrites*, FeS_2, and as the carbonate, $FeCO_3$, or *siderite*.

Iron is prepared by reduction of its oxides by carbon: —

$$Fe_2O_3 + 3\,C = 3\,CO + 2\,Fe;$$
$$Fe_3O_4 + 4\,C = 4\,CO + 3\,Fe.$$

In preparing iron on the commercial scale the *blast furnace* is employed. This is shown in Figure 59. The furnace consists of an iron case lined on the inside with fire-brick, and has the shape shown in the figure. It is provided with pipes at the bottom for introducing hot air under pressure, and with pipes at the top for carrying off the gaseous products of combustion. These furnaces are often quite large, being as much as eighty feet high. They are filled with coal or coke, the ore,

and a flux, which are mixed when introduced into the furnace. The nature of the flux which is used depends upon the impurities contained in the ore. If there is much silica in the ore, limestone is used as the flux. The flux generally employed is, indeed, limestone.

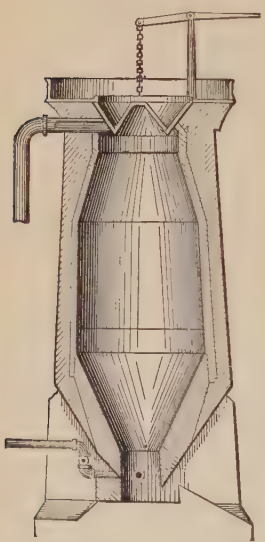

Fig. 59.

The oxide of iron is reduced to the metal by means of the highly heated carbon, and the carbon monoxide formed as the product of the combustion of the carbon. The combustion of the carbon is effected by blowing hot air under pressure into the bottom of the furnaces. Much of the carbon monoxide is not oxidized by the iron oxide to carbon dioxide, and escapes at the top of the furnace through tubes provided to receive it, and is used as fuel.

The operation of a blast furnace is continuous; alternate charges of coke, ore, and flux are being continually added at the top of the furnace, and the molten metal and slag drawn off at the bottom. The iron is run into moulds made in the sand, and this impure product is known as *pig-iron*, or *cast-iron*.

Properties of Iron. — Pure iron is light gray in color, can readily be drawn into wire, and hammered or rolled into sheets. At a bright red heat it can be *welded*, or one piece made to adhere to another by simply hammering the two together. Iron is one of the most resistant to strain of all the metals. It is this property, together with its great abundance and the ease with which it can be prepared, that makes it the most valuable commercially of all the metals.

When iron is heated in the presence of the air, it readily burns, uniting with oxygen and forming one of the oxides of

iron. Iron acts upon moist air even at ordinary temperatures, but acts slowly. This is known as the *rusting of iron.* Iron dissolves readily in dilute acids, liberating hydrogen and combining with the anion of the acid, forming the corresponding salt.

When iron is dipped into very strong nitric acid, and then into dilute, the latter is without action upon it. The iron is then in the *passive state.* This has recently been shown to be due to an electrical condition of the metal, and not to the formation of a protecting layer of oxide over its surface as was formerly supposed.

Impure or Commercial Iron. — The different varieties of iron which are used commercially have very different properties. These are due to the different amounts of impurities in the iron. We have already seen how *pig-iron* or *cast-iron* is made. Cast-iron is very impure, containing in addition to from 3 to 4 per cent of carbon, one or more per cent of silicon, besides phosphorus, manganese, sulphur, etc. If there is considerable silicon present, and the cast-iron cools slowly, the carbon separates largely as graphite, and gives a gray cast to the iron. This is known as *gray cast-iron.* If the iron is cooled rapidly, the carbon remains in chemical combination with the iron. Such iron is light in color and is known as *chilled cast-iron. White cast-iron* contains no graphite, and usually less silicon or more manganese or sulphur than gray cast-iron. Cast-iron is brittle and readily broken by a jar, and is far less tough than pure iron. Cast-iron is not malleable, since it is too brittle, and although it melts lower than pure iron, does not appreciably soften before it melts. It therefore cannot be welded like pure iron.

If the ore from which the iron is made is rich in manganese, the final product is also rich in manganese, and usually contains more carbon than ordinary cast-iron. This is known as *spiegel iron,* and contains from 10 to 15 per cent of manganese, and in some cases even more.

When most of the impurities have been removed from iron,

we have *wrought-iron*. This still contains a small amount of carbon, the amount, however, usually being less than one-half of one per cent. Wrought-iron has very different properties from cast-iron. It is very tough, strong, and malleable. It melts at about 2000°, but becomes soft at a bright red heat, so that it can be hammered, rolled, or welded. Wrought-iron, while extremely tough, is comparatively soft, and bends easily under strain. It is, therefore, not as useful as a form of iron which contains more carbon, and is known as steel.

Steel is usually iron practically free from all impurities except carbon, which is present to from 0.8 to 2 per cent. There are two general methods by which steel may be made,— either by removing carbon and other impurities from cast-iron, or by adding carbon to wrought-iron. The former process would seem to be the simpler, since it is necessary to remove the carbon from cast-iron in order to obtain wrought-iron. The latter process, however, is the one most frequently made use of. A few methods of making steel are so important commercially, and are so frequently referred to that they will be briefly described.

The Bessemer Converter consists of a pear-shaped vessel of malleable iron, lined on the inside with refractory material. The molten cast-iron is poured into the converter, and compressed air forced through the molten metal. The carbon and silicon are completely oxidized by the oxygen of the air, and the product is similar in composition to wrought-iron. This is kept above its melting-point by the heat of combustion of the carbon and silicon. In order to obtain a product with the desired amount of carbon, spiegel iron is added in quantity sufficient to bring the percentage of carbon up to the desired amount. The product is *Bessemer steel*, which has found such extensive application in the arts.

The Thomas-Gilchrist Converter. — The Bessemer process of making steel does not remove the phosphorus from the iron. The presence of an appreciable amount of phosphorus so changes the properties of the steel as to render it entirely

unfit for certain purposes. While they were dependent solely upon the Bessemer or similar processes, only certain iron ores which contain only a small amount of phosphorus, could be used for making steel. This has largely been changed, due to the Thomas-Gilchrist converter. This is essentially a Bessemer converter lined with burned dolomite, which is a mixture of lime and magnesia. This *basic lining*, as it is termed, unites with the phosphoric acid formed by the oxidation of the phosphorus by the oxygen of the air which is blown through the molten iron, and forms calcium and magnesium phosphates. This material, known as the *Thomas slag*, is extensively used as a source of phosphoric acid in commercial fertilizers, having a composition very similar to the "phosphate rock," which is so extensively used as a fertilizer.

Steel is useful largely because it can be made to assume any degree of hardness. When allowed to cool very slowly, ordinary steel is soft and resembles wrought-iron in its properties. When highly heated and made to cool rapidly it becomes very hard and brittle, the degree of hardness depending somewhat upon the amount of carbon present. The process by which the hardness of steel is regulated is known as *tempering*. The steel is heated moderately, the temperature being estimated by the color of the layer of oxide which forms on the bright surface. The steel is then cooled more or less slowly.

Ferrous and Ferric Compounds. — Iron forms two kinds of ions, — the one carrying two electrical charges and known as the *ferrous ion*, $\overset{++}{\mathrm{Fe}}$, and the other carrying three electrical charges and known as the *ferric ion*, $\overset{+++}{\mathrm{Fe}}$. These are what have hitherto been described as the ferrous and the ferric condition. In the case of iron we can verify the statement that *Faraday's law* is *the base of chemical valence*. If a given electric current is passed through a solution of a ferrous, and a solution of a ferric, salt, one and one-half times as much iron will separate from the ferrous solution as from the ferric. By comparing the amount of iron which separates from a ferrous solution

with the amount of a univalent metal separated by the same current, it can be shown that the ferrous ion ($\overset{++}{Fe}$) is bivalent, or carries two charges of electricity. The ferric ion ($\overset{+++}{Fe}$) is, therefore, trivalent, or carries three charges of electricity.

We shall see that a ferrous ion can be converted into a ferric ion by oxidation, as it is said, and a ferric ion converted into a ferrous ion by reduction. All that takes place when a ferrous ion is converted into a ferric ion is the addition of one electrical charge, and the removal of one electrical charge from a ferric ion converts it into a ferrous ion. *Oxidation and reduction as used in this sense are simply the addition or removal of electrical energy, and, like valence, have their physical basis in Faraday's law.*

Ferrous ($Fe(OH)_2$) and Ferric ($Fe(OH)_3$) Hydroxides. — The two conditions described above are exemplified in the hydroxyl compounds of iron. In one of these the iron holds two hydroxyl groups in combination; in the other, three. Ferrous hydroxide is precipitated when an alkali is added to a solution of a ferrous salt: —

$$FeCl_2 + 2\,NaOH = 2\,NaCl + Fe(OH)_2.$$

Ferric hydroxide is formed when an alkali is added to a solution of a ferric salt: —

$$FeCl_3 + 3\,NaOH = 3\,NaCl + Fe(OH)_3.$$

Iron forms two well-known oxides, Fe_2O_3, or *hematite*, and Fe_3O_4, or *magnetite*.

Ferrous ($FeCl_2$) and Ferric ($FeCl_3$) Chlorides. — Ferrous chloride is obtained when an excess of iron is treated with hydrochloric acid. It forms crystals containing four molecules of water, $FeCl_2 . 4\,H_2O$.

Ferric chloride is formed by passing chlorine over iron. It is also formed by passing chlorine into a solution of ferrous chloride.

Sulphides of Iron. — When iron filings and sulphur are heated together, the two combine and form *ferrous sulphide*, FeS. It is

also formed by the action of ammonium sulphide on a ferrous salt. Treated with acids, hydrogen sulphide is liberated. Two other sulphides of iron exist.

Ferrous Sulphate, $FeSO_4 . 7\ H_2O$. — Ferrous sulphate, also called *iron vitriol* on account of its composition, or *green vitriol* on account of its color, is the most important ferrous compound. It is formed by the action of sulphuric acid on iron or iron sulphide. It is made commercially by allowing ferrous sulphide to take up oxygen from the air: —

$$FeS + 2\ O_2 = FeSO_4.$$

The salt is then extracted with water. Ferrous sulphate forms light green crystals, and is extensively used in dyeing, in pharmacy, and as a disinfectant.

Ferric Sulphate, $Fe_2(SO_4)_3$, is formed by dissolving ferric oxide or hydroxide in sulphuric acid: —

$$2\ Fe(OH)_3 + 3\ H_2SO_4 = Fe_2(SO_4)_3 + 6\ H_2O.$$

It is also formed by the addition of a half-equivalent of sulphuric acid to ferrous sulphate, in the presence of an oxidizing agent like nitric acid. Ferric sulphate forms double sulphates with the alkali sulphates, which, in composition and crystalline form, resemble the aluminium alums, and are termed *iron alums.*

Potassium Ferrocyanide, $K_4Fe(CN)_6$. — Although iron does not combine directly with the cyanogen ion and form cyanides, it forms double cyanides which are beautifully crystallized compounds. When potassium cyanide is allowed to act upon iron in the presence of water, the following reaction takes place: —

$$Fe + 6\ KCN + 2\ H_2O = 2\ KOH + H_2 + K_4Fe(CN)_6.$$

Potassium ferrocyanide is usually formed by heating nitrogenous matter with iron filings and potash. When the mass is digested with water and the solution evaporated, beautiful yellow crystals are formed having the composition $K_4Fe(CN)_6 . 3\ H_2O$. This is potassium ferrocyanide, known commercially as *yellow prussiate of potash.*

Potassium Ferricyanide, $K_3Fe(CN)_6$, is formed by the action of oxidizing agents on potassium ferrocyanide. If chlorine is passed into a solution of potassium ferrocyanide, potassium ferricyanide is formed: —

$$2\,K_4Fe(CN)_6 + Cl_2 = 2\,KCl + 2\,K_3Fe(CN)_6.$$

The compound $K_3Fe(CN)_6$ is known also as *red prussiate of potash*, from the deep red color of its crystals.

Change in Color with Change in Electrical Charge. — An ion having the same chemical composition does not always have the same color. Take the ion $Fe(CN)_6$; in potassium ferrocyanide it is yellow and gives the yellow color to a solution of this salt. The ion in this case is formed by the dissociation of the salt $K_4Fe(CN)_6$: —

$$K_4Fe(CN)_6 = \overset{+}{K},\ \overset{+}{K},\ \overset{+}{K},\ \overset{+}{K},\ Fe(\overset{\equiv}{C}N)_6.$$

The ion $Fe(\overset{\equiv}{C}N)_6$ carries four negative charges. The ion $Fe(CN)_6$, obtained by the dissociation of potassium ferricyanide, is red. The compound $K_3Fe(CN)_6$ dissociates as follows: —

$$K_3Fe(CN)_6 = \overset{+}{K},\ \overset{+}{K},\ \overset{+}{K},\ Fe(\overset{=}{C}N)_6.$$

The ion $Fe(\overset{=}{C}N)_6$, in this case, carries three negative charges, and the difference of one charge changes the color of the ion from yellow to red.

To take a simpler example: The iron ion in the ferrous condition, $\overset{++}{Fe}$, is green, as is seen in solutions of ferrous salts; while the iron ion in the ferric condition, $\overset{+++}{Fe}$, is yellow, as is seen in solutions of ferric salts. A large number of examples of changes in the color of ions with change in the electrical charge which they carry, might be given.

COBALT (At. Wt = 59.0)

The mineral *smaltite*, which is the arsenide of the composition $CoAs_2$, and the mineral *cobaltite*, which has the composition

CoAsS, are important. The element is prepared by reducing the oxide either with highly heated carbon, or with hydrogen. Cobalt resembles iron in many respects.

Cobaltous and Cobaltic Compounds. — Cobalt, like iron, forms two kinds of ions, — the cobaltous ion $\overset{++}{Co}$, and the cobaltic ion $\overset{+++}{Co}$. Unlike iron, however, the cobaltous ion is the more stable condition, while the ferric condition is the more stable for the iron ion. The cobaltous ion combines readily with the anions of acids, forming solutions of cobalt salts.

Oxides and Hydroxides of Cobalt. — Several oxides of cobalt are known. *Cobaltous oxide*, CoO, is formed when cobaltous carbonate or hydroxide is heated. It is a greenish powder, easily reducible to the metal. *Cobaltic oxide*, or *cobalt sesquioxide*, Co_2O_3, is formed by gently heating the nitrate.

When a cobaltous salt is treated with an alkali, cobaltous hydroxide is formed: —

$$CoCl_2 + 2\ KOH = 2\ KCl + Co(OH)_2.$$

Cobaltous Salts. — When metallic cobalt is heated in chlorine, *cobalt chloride*, $CoCl_2$, is formed. This crystallizes from an aqueous solution with six molecules of water — $CoCl_2 . 6\ H_2O$. The solution of the salt is red. When the water is removed, the salt is deep blue in color, due to the driving back of the ions into molecules, which are blue. Cobalt chloride has, therefore, been used as *sympathetic ink*. When a solution of the salt is used for writing on paper, the writing is practically colorless, due to the nearly colorless nature of an aqueous solution of cobaltous chloride.

When the paper is warmed the blue color appears, and the writing becomes plainly legible. When the blue material is allowed to stand in contact with the air, it takes up moisture, becoming again invisible.

NICKEL (At. Wt. = 58.7)

An element which resembles cobalt in many respects is nickel. It occurs in nature chiefly in combination with arsenic, NiAs, as *niccolite*. The silicate occurs in abundance and is known as *garnierite*.

Nickel is prepared by reducing the oxide with carbon at a high temperature, and by reducing the oxide in a stream of hydrogen.

On account of its resistance to oxidation, nickel is extensively used to cover metals which are more readily oxidized, such as iron, etc. The nickel is deposited upon the iron electrolytically. This method of covering one metal with another is known as *electroplating*.

Nickel forms valuable alloys with a number of the metals. *German silver* is an alloy of nickel with zinc and copper. Alloys of nickel and copper are used as coins; our so-called *nickel* containing 75 per cent copper and 25 per cent nickel.

Compounds of Nickel. — While there are a few compounds known in which nickel plays the rôle of a trivalent element, it is almost always present as the bivalent ion $\overset{++}{\text{Ni}}$. The *oxide* of nickel, NiO, is formed as a black powder when the hydroxide is heated in a limited supply of air. When there is an abundant supply of oxygen, the *sesquioxide*, Ni_2O_3, is formed.

The green *hydroxide*, $Ni(OH)_2$, is formed when a solution of a nickel salt is treated with a solution of a hydroxide: —

$$NiCl_2 + 2\,KOH = 2\,KCl + Ni(OH)_2.$$

EXPERIMENTS WITH IRON, COBALT, AND NICKEL

Experiment 171. Preparation of Ferrous Chloride. — (Iron wire or iron filings; hydrochloric acid.)

Treat 5 grams of iron wire or iron filings with 15 cc. of dilute hydrochloric acid. Smell the odor of the escaping gases.

Treat a little of the ferrous chloride with sodium hydroxide. Ferrous hydroxide is precipitated. What is its color? As it stands in contact with the air it passes over into ferric hydrox-

ide. Note the changes in color which it undergoes as it passes from the practically white ferrous hydroxide to the reddish brown ferric hydroxide.

Treat a little ferrous chloride with a little concentrated nitric acid and boil the solution. The ferrous ion is gradually transformed into the ferric ion. Note the change in the color of the solution. This same transformation is effected by passing chlorine through the solution. (See page 277.)

Experiment 172. Properties of Ferrous Salts. — (Ferrous sulphate; potassium ferricyanide.)

Treat a solution of potassium ferricyanide with a few drops of a solution of ferrous sulphate. A deep blue precipitate is formed, — *Turnbull's blue.* Perform the same experiment, using potassium ferrocyanide. A light blue color is produced.

Treat a solution of ammonium sulphocyanate with a solution of a ferrous salt. If there is no ferric salt present in the ferrous salt, the solution of the sulphocyanate will not change color. This is secured by boiling the solution *just before using* with a little iron or zinc and hydrochloric acid. (See page 277.)

Experiment 173. Separation of Ferric Chloride; Properties of Ferric Salts. — (Iron wire or iron filings; hydrochloric acid; nitric acid.)

Prepare ferric chloride as at the end of Experiment 171. Dissolve the iron in hydrochloric acid. Add nitric acid and boil the solution. Repeat the addition of nitric acid and the boiling two or three times to transform all of the ferrous compound into the ferric condition.

Add to a little of the ferric chloride a solution of potassium ferrocyanide. A characteristic blue precipitate is formed, — *Berlin or Prussian blue.*

Add a few drops of ferric chloride to a solution of potassium sulphocyanate. A characteristic blood-red color appears.

Add a few drops of a ferric salt to a solution of potassium ferricyanide; no blue color is produced. The solution turns brown. (See page 277.)

Experiment 174. Detection of a Ferrous and a Ferric Salt when Both are Present. — (Ferrous sulphate; ferric chloride.)

Mix a gram of ferrous sulphate with a gram of ferric chloride and test the mixture for ferrous and ferric iron.

Add to a few drops of the solution a solution of potassium ferricyanide. What does the blue color show?

Add a few drops of the solution to a solution of potassium ferrocyanide. What does the blue color indicate?

To a solution of potassium sulphocyanate add a drop of the solution of the mixed iron salts. The red color indicates the presence of iron in what condition?

State clearly and concisely the reactions for a ferrous salt? for a ferric salt? (See page 278.)

Experiment 175. Precipitation of Iron as the Sulphide. — (Ferrous sulphate; ferric chloride; hydrogen sulphide generator; ammonium sulphide.)

Into a solution of ferrous sulphate, and of ferric chloride, conduct hydrogen sulphide. What takes place?

To similar solutions of the same substances add ammonium sulphide. What is formed in each case?

Test the solubility of the precipitates in dilute acids?

Explain why hydrogen sulphide does not precipitate all of the iron from solutions of ferrous salts? (See page 278.)

Experiment 176. Sympathetic Ink. — (Cobalt chloride.)

Prepare a fairly concentrated solution of cobalt chloride. Write upon paper with this solution. Allow the paper to dry. Can anything be seen? Warm the paper carefully over the flame or on the air-bath. The characters come out in blue. Explain? (See page 281.)

Experiment 177. Action of Hydrogen Sulphide on Cobalt Salts. — (Cobalt chloride; hydrogen sulphide generator.)

Pass hydrogen sulphide into a solution of cobalt chloride. What is precipitated? Is it soluble in dilute acids? Add ammonia. What is formed? Explain?

Experiment 178. Action of Hydrogen Sulphide on Nickel Salts. — (Nickel chloride; hydrogen sulphide generator.)

Pass hydrogen sulphide into a solution of a nickel salt. What is formed? Test its solubility in dilute acids. Add ammonia. What is precipitated? Explain the difference between the action of hydrogen sulphide and of ammonium sulphide?

PROBLEMS

1. How much ferrous and ferric chlorides can be prepared from the iron contained in 3 grams of hematite? in 3 grams of magnetite?

2. Amounts of potassium ferrocyanide and potassium ferricyanide which contain 10 grams of iron?

3. Percentage of cobalt in the compound $CoCl_2 . 6\,H_2O$. Amount of water in 5 grams of this substance?

4. How much niccolite would be required to yield the nickel necessary to form 100 grams of nickel sulphide?

CHAPTER XXIII

MANGANESE, CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM, RADIUM

MANGANESE (At. Wt. = 55.0)

We now come to an element which probably forms as large a variety of compounds as any element known. This is due to the many degrees of valence which manganese can manifest.

Occurrence, Preparation, and Properties of Manganese.— Manganese occurs in nature in small quantities in the free condition, but usually as one of its oxides. The chief source of manganese is the oxide MnO_2, which is the mineral *pyrolusite*.

Manganese is prepared by heating the oxides with carbon in an electric furnace, also by electrolysis of the fused chloride, but more conveniently by mixing the oxide with finely divided aluminium and igniting the mixture. This is one of *Goldschmidt's mixtures*, the aluminium taking the oxygen, setting free the manganese.

Oxides of Manganese. — Manganese forms no less than seven compounds with oxygen. The one containing the smallest amount of oxygen is manganous oxide, MnO. This is formed by reducing the higher oxides in a stream of hydrogen, and by heating manganous hydroxide. Manganese sesquioxide, Mn_2O_3, occurs in nature as *braunite*. Manganous-manganic oxide, Mn_3O_4, is formed when the other oxides of manganese are heated in the air. Manganese dioxide, MnO_2, occurs in nature as *pyrolusite*, and is the most important ore of manganese. There exists a trioxide of manganese, MnO_3, and also a septoxide, Mn_2O_7. There also exists a tetroxide of manganese, MnO_4.

Arranging these oxides in the order of increasing amount of oxygen, we have: —

MnO	MnO_3
Mn_3O_4	Mn_2O_7
Mn_2O_3	MnO_4
MnO_2	

Manganous Salts. — The manganous ion, $\overset{++}{Mn}$, combines with the anions of acids, forming salts which are usually beautifully crystallized compounds. *Manganous chloride*, $MnCl_2 . 4\ H_2O$, is formed by the action of hydrochloric acid on manganese dioxide: —

$$MnO_2 + 4\ HCl = 2\ H_2O + Cl_2 + MnCl_2.$$

Manganic Compounds. — The manganic ion, $\overset{+++}{Mn}$, can unite with the anions of acids and form salts. The manganic salts are, however, not as numerous as the manganous, and in general not as stable, being strongly hydrolyzed by water.

Quadrivalent Manganese. — A few compounds are known in which tetravalent manganese apparently exists. This is the case with the oxide, MnO_2, and the hydroxide. The most important of these substances is manganese dioxide, which, as we have seen, formerly found extensive application in the preparation of chlorine, and to-day is largely used in the arts as an oxidizing agent.

It is also used in the construction of one of the most efficient forms of primary cells, the *Leclanché cell.*

Valence and Properties of Manganese. — It should be noted that as the valence of manganese increases, its basic nature rapidly diminishes. Bivalent manganese is distinctly basic, forming stable salts with the anions of acids. Trivalent manganese is very weakly basic, its salts being strongly hydrolyzed by water. Tetravalent manganese is scarcely basic at all, its compound with such a strong acid as hydrochloric being so unstable that its very existence is doubtful.

When we pass to manganese with higher valence, not only has all the basic nature been lost, but we find acid properties

beginning to manifest themselves, and the highest oxidation product of manganese is a strong acid. These acid compounds of manganese we shall now study.

Manganic Acid, H_2MnO_4. — We have already studied compounds of manganese in which this element has appeared in the capacity of a bivalent, trivalent, and quadrivalent ion. Pentavalent manganese is not known, but hexavalent manganese is well known, manifesting itself in salts of the compound, manganic acid, — the analogue of sulphuric acid. These are formed, as we would expect, by strongly oxidizing manganese in the presence of bases. *Potassium manganate*, K_2MnO_4, is formed by fusing potassium hydroxide with manganese dioxide in the presence of the oxygen of the air, or better, an oxidizing agent such as potassium chlorate. The manganese is oxidized from the quadrivalent to the sexivalent condition, the potassium chlorate being reduced to potassium chloride: —

$$3\ MnO_2 + KClO_3 + 6\ KOH = KCl + 3\ H_2O + 3\ K_2MnO_4.$$

This mass forms a green solution, from which green crystals of potassium manganate, K_2MnO_4, separate.

The following transformation is effected by carbon dioxide and consequently takes place slowly when a manganate is exposed to the air: —

$$3\ K_2MnO_4 + 2\ CO_2 = MnO_2 + 2\ K_2CO_3 + 2\ KMnO_4.$$

The change of color from the green manganate, through blue and purple to the purplish red permanganate, is very striking.

Permanganic Acid, $KMnO_4$. — The highest oxidation product of manganese containing hydrogen and oxygen is permanganic acid, $HMnO_4$, — the analogue of perchloric acid. The best method of preparing the acid consists in the electrolysis of the potassium salt of this acid. This method, which was devised by Morse, is carried out as follows: Two unglazed porcelain cups containing the one water to which a little alkali is added,

and the other water to which a little permanganic acid is added if available to make the water conducting, are immersed in a beaker containing a solution of potassium permanganate. The platinum electrodes are inserted the one in each cup, the cathode in the cup containing the alkali. The current is passed, when the potassium ions move toward the cathode, give up their charge, decompose water, and liberate hydrogen. The alkali formed around the cathode is easily siphoned off from time to time. The permanganic ions, $\overline{M}nO_4$, move to the anode, decompose water, forming permanganic acid and liberate oxygen. The permanganic acid collects in the cup around the anode, and after the current has been passed for a sufficient time, can be obtained in perfectly pure condition and in any quantity desired. Permanganic acid is a very strong acid.

Potassium permanganate, $KMnO_4$, is readily obtained by passing carbon dioxide through a solution of potassium manganate, as already described, or by treating a carbonate with permanganic acid. Its solution has exactly the same color as permanganic acid, — purplish red. It crystallizes in beautiful purple crystals.

Potassium permanganate is characterized chiefly by its oxidizing power.

CHROMIUM (At. Wt. = 52.1)

Chromium forms a number of series of compounds, and many of these are closely related to iron and manganese. It occurs in nature largely as chrome iron ore, which is *iron chromite*, having the composition $Fe(CrO_2)_2$.

Chromium is prepared most conveniently by heating the oxide with finely divided aluminium, according to the method of *Goldschmidt*.

Oxides of Chromium. — Chromium, like manganese, forms a number of oxides. *Chromous oxide*, CrO, is formed by reducing the higher oxides. *Chromic oxide* or *chromium sesquioxide*, Cr_2O_3, is formed by heating the trioxide. *Chromium trioxide*,

CrO_3, is formed by adding concentrated sulphuric acid to potassium dichromate in very concentrated solution: —

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2\,CrO_3.$$

It is a dark red, beautifully crystalline substance, characterized by its tremendous oxidizing power. When brought in contact with organic compounds, these are oxidized or burned up, as we say.

Valence and Properties of Chromium Ions. — It is obvious, from the composition of the oxides and hydroxides of chromium, that this element can exist in various conditions of valence. Bivalent chromium ions, Cr^{++}, are distinctly basic. The bivalent ions, however, readily pass into trivalent ions, Cr^{+++}, which are very weakly basic towards strong acids, and are acidic towards certain bases. This is strictly analogous to the ions of iron and manganese. Those of lower valence, or with the smaller electrical charge, are basic; but as the valence increases, or as the amount of electrical energy which they carry increases, the basic property becomes less and less, and acidic properties begin to manifest themselves. When the valence of the chromium ion reaches six, as in the compound H_2CrO_4, we have a very strong acid, *chromic acid*, and, similarly, when it reaches seven, in *perchromic acid*, $HCrO_4$. This is analogous to iron, and especially to manganese, where the sexivalent ion is acidic as in manganic acid, and the septivalent ion strongly acidic as in permanganic acid.

Chromic Acid, H_2CrO_4. — In composition this acid resembles sulphuric acid, manganic acid, and the like.

The compound H_2CrO_4 is, however, not known. When its salts are treated with sulphuric acid, the anhydride CrO_3 is obtained, which is chromic acid minus water: —

$$H_2CrO_4 - H_2O = CrO_3.$$

In this compound the chromium is obviously sexivalent, and with its high valence the strongly acid properties begin to come out.

Chromates. — Salts of this acid are formed when ferrous chromite is heated on the air in the presence of an alkali. The chromium is oxidized to the chromate, which is soluble, and the iron to ferric oxide, which is insoluble in water. The mixture is treated with water, when the chromate dissolves. If caustic potash is used, the resulting compound is *potassium chromate*. This is deep yellow in color, due to the color of the chromic acid ion $C\bar{\bar{r}}O_4$. It forms crystals which are isomorphous with potassium sulphate.

Dichromates. — When a chromate like potassium chromate is treated with an acid, the color of the solution changes from yellow to red. The reaction in the case of potassium chromate may be represented as follows: —

$$2\ K_2CrO_4 + H_2SO_4 = H_2O + K_2SO_4 + K_2Cr_2O_7.$$

Potassium dichromate, $K_2Cr_2O_7$, crystallizes from the solution in beautiful red crystals, which often grow to unusual size and are of unusual geometrical perfection. Potassium dichromate is a powerful oxidizing agent. It readily gives up oxygen, the chromium being reduced to the chromic condition.

When potassium dichromate is treated with caustic potash, potassium chromate is formed: —

$$K_2Cr_2O_7 + 2\ KOH = 2\ K_2CrO_4 + H_2O.$$

This is made evident by the change in the color of the solution from red to yellow. It will be observed that the valence of the chromium in potassium dichromate is the same as in potassium chromate. The change from the former to the latter by the addition of an alkali, and the reverse change by the addition of an acid, therefore, involve neither oxidation nor reduction.

URANIUM (At. Wt. = 238.5)

The three comparatively rare elements *molybdenum*, *tungsten*, and *uranium* also belong in this group.

Uranium is of special interest on account of its power of emitting a certain remarkable kind of radiation.

Uranium Radiation. — Compounds of uranium have the property of emitting an invisible radiation, which traverses many substances impervious to light, such as black paper, thin sheets of many metals, such as aluminium, copper, etc. This property is possessed by metallic uranium to from three to four times the extent that it is manifested by the salts of this metal.

This is entirely different from the phosphorescence shown by salts of uranium, since the latter disappears very quickly, while the power of emitting this invisible radiation persists for years.

If a piece of uranium or of one of its salts is placed above a photographic plate covered with black paper or aluminium leaf, and various substances interposed between the uranium and the plate, after several hours *radiographs* are obtained upon the plate.

Other radioactive substances are: *radium*, *polonium*, and *thorium*.

Radium (at. wt. 257.8). — One of the most remarkable of all the chemical elements is *radium*, discovered recently in pitchblende. It forms salts with acids which are of perfectly definite composition, and thus resembles the metals. It has the power of giving off several kinds of radiation, some of which can readily pass through objects opaque to light. The most remarkable properties, however, of this remarkable substance are the following: It is constantly giving off heat; and it yields helium as one of its decomposition products. Radium gives off a very appreciable amount of heat energy, maintaining itself at a temperature which is a degree or two above the surrounding medium; indeed, radium bromide gives off enough heat to melt its own weight of ice every hour. This continuous production of heat energy is probably due to a shrinking of the radium atom, analogous to the shrinking of the sun.

The formation of helium from radium is of the very greatest interest and importance, since it is the first well-established case of the *transformation of one chemical element into another, or of the formation of one chemical element from another.*

EXPERIMENTS WITH MANGANESE AND CHROMIUM

Experiment 179. Reaction of Manganese Salts. — (Soluble salts of manganese; ammonia; sodium hydroxide; hydrogen sulphide generator; ammonium sulphide.)

Treat solutions of manganese salts with ammonia. What is precipitated? Add sodium hydroxide to solutions of manganese salts. What is precipitated? Is it soluble in an excess of sodium hydroxide? How does manganese differ in this respect from aluminium?

Pass hydrogen sulphide into solutions of manganese salts. Is any precipitate formed?

Add ammonium sulphide to solutions of manganese salts. What is precipitated? What is the color of the precipitate? Is it soluble in dilute acids? Why is a manganese salt not precipitated by hydrogen sulphide?

Experiment 180. Preparation of Potassium Manganate. — (Porcelain crucible; manganese dioxide; potassium hydroxide; potassium chlorate.)

Mix 3 grams of finely powdered manganese dioxide with 3 grams of potassium hydroxide and add 2 grams of potassium chlorate. Heat the mixture. It will turn green, due to the formation of potassium manganate. Write the equation for the reaction?

Dissolve the green mass in a little water, and pass carbon dioxide through the solution. It will gradually become purple in color. This is due to the oxidation of the manganate to the permanganate. This same transformation is effected by allowing the crystals of the manganate to stand exposed to the air. (See page 287.)

Experiment 181. Color of Potassium Permanganate. — (Potassium permanganate; dilute sulphuric acid.)

When potassium permanganate dissolves in water, it dissociates thus: —

$$KMnO_4 = \overset{+}{K},\ \overset{-}{MnO_4}.$$

We naturally ask to which ion the beautiful color of the solution is due. It may be due to both.

That it is not due to the potassium ion is shown by the fact that solutions of such potassium salts as the chloride, nitrate, sulphate, etc., are colorless. These yield in solution large numbers of potassium ions, and yet their solutions are colorless. The color must be due to the $\dot{M}\bar{n}O_4$ ion.

Treat a solution of potassium permanganate with dilute sulphuric acid. Permanganic acid, $HMnO_4$, is formed. This dissociates as follows: —

$$HMnO_4 = \dot{H},\ \dot{M}\bar{n}O_4.$$

Explain why permanganic acid in solution has the same color as potassium permanganate. (See page 287.)

Experiment 182. Oxidizing Power of Potassium Permanganate. — (Potassium permanganate; oxalic acid; potassium sulphite; sulphuric acid; ferrous sulphate.)

To a dilute, warm solution of oxalic acid to which sulphuric acid has been added, add a solution of potassium permanganate, drop by drop. The color of the permanganate will disappear as long as there is any oxalic acid present. The oxalic acid is oxidized to water and carbon dioxide, and the latter is seen to escape from the solution. The manganese is reduced to the bivalent condition, and forms manganous sulphate.

Add sulphuric acid to a solution of potassium sulphite. Sulphurous acid is set free in the solution. Add potassium permanganate, drop by drop. The sulphurous acid is oxidized to sulphuric acid, and the manganese reduced as in the above experiment.

Add sulphuric acid to a dilute solution of ferrous sulphate, and then add potassium permanganate, drop by drop. The color instantly disappears on coming in contact with the ferrous salt. The ferrous sulphate is oxidized to ferric sulphate, and the permanganate reduced.

Add a drop of potassium permanganate to the end of your finger. The organic matter is oxidized, and the stain of oxide of manganese shows that the permanganate has been reduced. The stain can be readily removed by adding a drop of sulphurous acid. (See page 288.)

Experiment 183. Formation of Chromium Trioxide. — (Potassium dichromate; concentrated sulphuric acid.)

Fill a test-tube one-third full of potassium dichromate and cover the crystals with water. Warm carefully. When no

more of the salt will dissolve, pour the solution into a second test-tube and add carefully, drop at a time, concentrated sulphuric acid. Red crystals of chromium trioxide will separate. *These must not be allowed to come in contact with the hand.* Filter the solution through *glass wool* (not filter-paper). By means of a porcelain spatula remove a few of the crystals and lay them upon filter-paper. What occurs? Treat a few of the crystals with a little hydrochloric acid and warm. Smell the gas given off. Explain? (See page 289.)

Experiment 184. Chromates and Dichromates. — (Potassium chromate; potassium dichromate; silver nitrate; lead nitrate; sulphuric acid; hydrochloric acid.)

Dissolve 25 grams of potassium chromate in a little water and add sulphuric acid. The solution changes from yellow to red. Evaporate the solution, and beautiful red crystals of potassium dichromate separate. Write the equation for the above reaction?

Treat a solution of potassium dichromate with caustic potash, and the color changes from red to yellow. Explain? Write the equation for the above reaction?

Add a solution of potassium chromate to a solution of a salt of a heavy metal. The chromate of the metal is precipitated. The chromate of the metal is also precipitated when a solution of a dichromate is used instead of the chromate. Write equations for the reaction between potassium chromate and lead nitrate; for the reaction between potassium chromate and silver nitrate.

Note the color of the precipitates in the two cases? (See page 290.)

Experiment 185. Oxidizing Power of the Chromates and Dichromates. — (Potassium chromate; potassium dichromate; concentrated hydrochloric acid.)

Treat a solution of potassium chromate and of dichromate in separate test-tubes with concentrated hydrochloric acid. Heat the solutions. What evidence have you that the hydrochloric acid is oxidized? Is there any evidence that the chromate and dichromate are reduced?

To a solution of potassium dichromate in a test-tube add concentrated hydrochloric acid and a little alcohol. The solution quickly turns green, showing that the chromium has been reduced to the trivalent or chromic condition. Smell the odor of the escaping vapor. This is the odor of aldehyde formed by the oxidation of the alcohol. (See page 290.)

Experiment 186. Action of Reagents on Chromic Chromium. — (Potassium chromium alum; sodium hydroxide; potassium carbonate; ammonium sulphide.)

Potassium chrome alum or potassium chromium sulphate, $KCr(SO_4)_2$, is the analogue of potassium aluminium sulphate, $KAl(SO_4)_2$. It is obvious that in the above compound the chromium is in the chromic or trivalent condition.

When potassium chromium sulphate is treated with sodium hydroxide, chromium hydroxide is precipitated. Write the equation?

Addition of more sodium hydroxide dissolves the precipitate. Write the equation? Is this similar to the behavior of aluminium hydroxide?

Boil the solution; the chromium hydroxide is reprecipitated. Is this analogous to aluminium?

Treat another portion of the solution of chrome alum with sodium carbonate. Chromium hydroxide is precipitated. Write the equation? It is exactly analogous to aluminium. Treat still another portion of the solution of the chromium alum with ammonium sulphide. Chromium hydroxide is precipitated, since the sulphide is decomposed by water. Write the equation from the analogy to aluminium?

PROBLEMS

1. How much potassium manganate and how much potassium permanganate contain the same amount of manganese as 2 grams of manganite?

2. Amount of potassium chromate and of potassium dichromate obtainable from 10 grams of the oxide, Cr_2O_3?

CHAPTER XXIV

COPPER, SILVER, GOLD

COPPER (At. Wt. = 63.6)

There still remain three elements in the first group of the Periodic System which have not thus far been studied. These are copper, silver, and gold.

Occurrence and Preparation of Copper. — Copper occurs in considerable quantity in the free condition. It occurs in large quantities as cuprous oxide, Cu_2O, or *cuprite*; cupric oxide; *azurite* and *malachite* the blue and green basic carbonates; and *chalcopyrite*.

Copper is prepared from the oxides very simply by heating with charcoal.

Copper is finally purified by means of electrolysis. The impure copper is moulded into the form of large, thick plates, known as the *anode plates*. These are suspended in a large bath of copper sulphate, and are made the anodes by connecting them with the positive pole of a dynamo. Between these plates are alternately suspended thin sheets of pure copper, which are the cathodes, and these are connected with the negative pole of the dynamo. When the current is passed, copper is deposited upon each of the cathodes, and dissolves from each of the anodes. The action of the current is really to carry the copper from the anode to the cathode opposite to it, and deposit it upon the cathode.

Under these conditions the impurities are not deposited with the copper, but either remain in solution or are deposited in the form of a viscous mass on the bottom of the copper sulphate bath.

Properties of Copper. — Copper differs in color from all other metals, being a peculiar shade of red known as copper-red.

Copper is quite resistant to chemical reagents. In contact with moist air it becomes covered with a green basic carbonate. When heated in the air, it forms the oxide.

Copper is easily attacked by sulphur compounds, forming the sulphide.

On account of its physical properties, copper is one of the most valuable of the metals. It can be readily hammered into thin sheets or drawn into wire, and is very strong.

Next to silver, copper is the best conductor of electricity, and is extensively used in this capacity in connection with telegraphy and telephony, and especially in connection with electric lighting and electrotraction, where large amounts of electrical energy must be transported. This is one of the most important uses of the element copper.

Alloys of Copper. — With the metals copper forms a number of alloys which are very valuable. One of the best known is *brass*, which is an alloy of copper and zinc, containing generally about twice as much copper as zinc; but this varies greatly from one specimen to another. *German silver* or *argentan*, as we have seen, is an alloy of copper, nickel, and zinc. Copper also forms alloys with nickel and silver. These are frequently used for *coins*. The silver coins usually contain about ten per cent of copper.

Among the best-known alloys of copper are the *bronzes*. The ordinary bronzes are alloys of copper and tin, containing from 10 to 30 per cent of tin. Among the alloys of copper and tin are *bell metal* and *gun metal*.

Oxides of Copper. — Copper forms two compounds with oxygen, — *cuprous oxide*, Cu_2O, and *cupric oxide*, CuO. These are types of the two classes of copper compounds, — the *cuprous compounds*, in which copper is univalent, and the *cupric compounds*, in which the copper is bivalent. Copper, therefore, forms two kinds of ions, — the cuprous ion, $\overset{+}{Cu}$, and the cupric ion, $\overset{++}{Cu}$. Of these the cupric condition, in which the copper carries two electrical charges, is the more stable.

Copper Sulphate, $CuSO_4 . 5\ H_2O$. — This is the best known of all the compounds of copper, and one of the best-known substances. Copper sulphate, or *blue vitriol*, as it is called, is formed when sulphuric acid acts on metallic copper. The hydrogen is not set free but acts on more sulphuric acid, reducing it to sulphur dioxide: —

$$Cu + H_2SO_4 = CuSO_4 + H_2;$$

$$H_2SO_4 + H_2 = 2\ H_2O + SO_2.$$

Copper sulphate crystallizes from the solution in the form of beautiful blue crystals, containing five molecules of water — $CuSO_4 . 5\ H_2O$. When the sulphate is heated, it loses four molecules of water at 100°, but the fifth is retained until 200° is reached.

Precipitation of Copper by Zinc and Iron. — When a bar of zinc or iron is immersed in a solution of a copper salt, copper is precipitated upon the zinc or iron and the zinc or iron dissolves. When zinc replaces copper from its salts, the zinc atom takes the charge from the copper ion, becoming itself an ion, while the copper is converted into an atom: —

$$Zn + \overset{++}{Cu},\ \overset{=}{SO_4} = Cu + \overset{++}{Zn},\ \overset{=}{SO_4}.$$

SILVER (At. Wt. = 107.93)

We now come to the so-called *noble metals* or *precious metals*. The well-known elements silver and gold will now be studied.

Silver is not among the rare elements. It occurs in nature in considerable abundance and in a number of compounds. An important ore is the sulphide Ag_2S, *argentite*.

Preparation of Silver. — A large number of methods have been devised and used for obtaining pure silver. The method employed depends upon the nature of the silver ore which is being used.

When silver is set free along with many other substances, it

is frequently dissolved in mercury and the mercury then distilled off. This is known as the *amalgamation process.*

Lead ores, especially galena, usually contain silver, and silver is frequently obtained mixed with lead. The solution of silver in lead is concentrated by allowing it to crystallize. Pure lead separates at first, and the remaining solution becomes richer and richer in silver. A concentration of the silver in the lead is finally attained, where the crystals which separate have the same concentration of silver as the remaining solution.

When this stage is reached, it is impossible to effect further separation by crystallization. The above process of fractional crystallization can be continued until the solution contains about one per cent of silver.

To effect further separation the lead solution of silver is heated on the air. The lead is oxidized to litharge, and allowed to flow away or be absorbed by the porous walls of the cupel in which the oxidation takes place. This process is known as *cupellation.*

Properties of Silver. — Silver is a white metal and has a high lustre. It is not as hard as copper, and of all the metals is the best conductor of heat and electricity. It can be easily drawn into wire or hammered into thin foil.

Silver is not easily attacked by chemical reagents. It is not attacked by the strongest alkalies even when hot, nor by dilute acids, with the exception of nitric acid.

Silvering. — Silver, as we have seen, is quite resistant to ordinary chemical agents. It is consequently used for making utensils and objects of ornament. These are, however, expensive, and *silver-plated* wares are much used in their stead. These consist of brass, copper, or other metallic objects covered completely with metallic silver. They, therefore, have the properties of silver objects.

Silver-plating finds extensive application. The silver is deposited by a number of methods; the silver is reduced directly upon the object to be plated, or it is applied mechanically and pressed upon the object while hot. Another method which

is extensively used is the electrolytic. Silver is deposited electrolytically from a solution of the cyanide dissolved in potassium cyanide.

Silver is now being extensively deposited upon glass in the construction of *mirrors*.

Oxides and Hydroxide of Silver. — Silver forms three compounds with oxygen, — the suboxide, Ag_4O, the normal oxide, Ag_2O, and the superoxide, AgO. It, however, forms only one hydroxide, AgOH, which is stable only at very low temperatures.

The silver ion is univalent, combining with the anions of acids and forming salts of the general type, AgCl, $AgNO_3$, Ag_2SO_4, etc.

The silver ion is especially a reagent for the halogen ions. It combines with them, forming stable, insoluble compounds, which we shall now study.

Silver Chloride, AgCl, is formed whenever a silver ion comes in contact with a chlorine ion: —

$$\overset{+}{Ag} + \overset{-}{Cl} = AgCl.$$

It is a white precipitate, which quickly darkens when exposed to the light.

Silver chloride is practically insoluble in water, and is consequently used to determine quantitatively both silver and chlorine. It is readily soluble in aqueous ammonia, and is thus distinguished from the bromide and iodide.

Silver Bromide, AgBr. — Silver bromide is precipitated when silver ions come in contact with bromine ions: —

$$\overset{+}{Ag} + \overset{-}{Br} = AgBr.$$

Silver bromide is white with a slightly yellowish tint; is soluble with difficulty in ammonia and almost insoluble in water. Silver bromide is even more sensitive to light than silver chloride, and upon this fact is based its use in photography.

Photography. — The science of photography is based almost exclusively upon the action of light on silver bromide. The *sensitive film* is prepared by adding ammonium bromide to gelatine, and then adding silver nitrate in the dark. The following reaction takes place: —

$$NH_4Br + AgNO_3 = NH_4NO_3 + AgBr.$$

The silver bromide is distributed through the gelatine in a very fine state of division. The mass is then poured upon the surface of glass plates, to which it adheres in the form of a thin film.

The plate containing the film is then exposed to the action of the light from the object which it is desired to photograph. The time of the exposure depends upon the intensity of the light, and the sensitiveness of the film. The action of the light is probably to reduce the silver bromide to a sub-bromide of silver, although this is not proved.

The exposed plate is now treated with a *developer*, which consists of some reducing agent, such as pyrogallic acid, ferrous sulphate, etc. The object of the developer is to reduce the silver bromide depositing metallic silver, and the whole science of photography depends upon the fact that the silver bromide which is most strongly illuminated is most readily reduced by the developer. Where the object was brightest, the plate is covered with a deeper film of metallic silver, which becomes less and less dense as the illumination is less and less. The result is a photograph of the object with the light parts dark and the dark parts light. This is the so-called "negative." The negative thus obtained still contains unreduced silver bromide, since the portion of the salt which was not exposed to the light is not reduced by the developer. If the negative is exposed to the light in this condition, the silver bromide would be acted upon, and the original picture would be destroyed. To avoid this the negative must be *fixed*, *i.e.* treated with a solution of a substance which will dissolve the unreduced silver bromide. The fixing agent usually employed is a solution of sodium thiosulphate, $Na_2S_2O_3$, known technically as *hyposul-*

phite, or even as *hypo*. This acts upon the silver bromide, forming a double salt, which is quite soluble in water and is easily removed when the plate is washed with running water. The negative is now "fixed," and ready to be used in making *prints* or *positives*. A "positive picture," or a photograph proper, is obtained by placing the negative above paper covered with the sensitive film, and exposing it to light. The dark parts of the negative cut off the light and appear bright on the positive picture, and, conversely, the light parts appear dark, since much light passes through and acts upon the sensitive film upon the paper. The positive, therefore, represents the lights and shades in the order in which they occur in the object, and is a true picture in metallic silver of that object.

In some cases the print is immersed in a bath containing a gold or platinum salt, when the silver precipitates the gold or platinum, itself passing into solution. Such photographs have, then, the soft brown color of finely divided gold, or the harder steel-gray tint of finely divided platinum.

Silver Iodide, AgI, is formed whenever silver and iodine ions come in contact. It is a yellow solid, insoluble in water and in ammonia. Silver iodide, like the bromide and chloride, is sensitive to light, and was formerly used in connection with photography. Indeed, the earliest method of preparing photographs, devised by *Daguerre*, made use of silver iodide.

GOLD (At. Wt. = 197.25)

The element gold is one of the "noble metals," and is frequently classed with platinum and allied elements. On the whole, however, it seems best to study gold in connection with copper and silver.

Gold occurs in nature chiefly in the uncombined condition, in the form of nuggets or grains in quartzite rocks or in sands. It also occurs combined with the element tellurium, as the telluride. When it occurs native, it is by no means pure, containing silver, copper, etc.

The Metallurgy of Gold. — Gold occurs usually in very small quantities, and widely distributed through a large mass of rock or sand. It must be obtained free from large quantities of foreign substances. This is accomplished by *placer mining*. In placer mining the earth or sand is washed with water, the light materials being carried away and the gold left behind with the heavier substances. In *hydraulic mining* the gold-bearing earth and sands are washed down from the hills by water under pressure, and the heavy gold collected by dissolving it in mercury. The gold is obtained from the amalgam by distilling off the mercury.

If certain impurities are present, the *cyanide process* is used. This consists in treating the gold ore with potassium cyanide, in which finely divided gold readily dissolves. The gold is precipitated from the cyanide solution by means of metallic zinc, or electrolytically, and then subjected to cupellation. Gold thus obtained is impure and must be *purified*. The silver can be removed by dissolving it out in nitric or concentrated sulphuric acid. If the amount of gold in the alloy exceeds 25 per cent, this does not work satisfactorily. In such cases the alloy is fused with enough silver to dilute the gold to not more than one-fourth. The process is therefore called *quartation*.

Properties of Gold. — Gold is a soft, yellow solid, melting at 1064°, and forming a greenish liquid. It has a very high specific gravity, — 19.3. Gold is extremely malleable, and can be hammered into leaves not more than two-millionths of a millimetre in thickness. Such gold leaf is translucent and has a green color.

Gold is very resistant chemically, being attacked by comparatively few substances.

The solution of gold in chlorine water is of special interest. When the molecules of gold come in contact with the molecules of chlorine, the former become cations and the latter anions: —

$$Au + Cl + Cl + Cl = \overset{+++}{Au}, \overset{-}{Cl}, \overset{-}{Cl}, \overset{-}{Cl}.$$

Gold forms *alloys* with a number of the metals. The best known and the most important are the alloys with copper and silver. Pure gold is too soft for use either as coin or as ornamental objects. To make it harder and more durable, copper is added. This gives to the gold a deep red color. The alloy containing 10 per cent of copper is frequently used. The purity of the gold is expressed in *carats*, pure gold being 24 carats. The number of carats means the number of parts of gold in 24 parts of the alloy. Thus, 18-carat gold means an alloy containing 18 parts gold and 6 parts copper.

The alloy of gold and silver is extensively used instead of pure gold, being more resistant to abrasion and more durable.

Gold-plating. — Metal objects are covered with gold in the same manner and for the same purpose that they are covered with silver. Gold-plating has been effected by a number of methods, but these have practically all given way to the electrical. The object to be electroplated with gold is made the cathode, and a piece of pure gold the anode, the double cyanide of gold and potassium being the electrolyte.

Oxides and Hydroxides of Gold. — Gold forms the two oxides Au_2O and Au_2O_3, which are typical of the univalent and trivalent compounds of gold. It also forms the corresponding hydroxides, $Au(OH)$ and $Au(OH)_3$. Although these compounds are weak bases, combining with the anions of certain acids and forming salts, the auric hydroxide also has acid properties.

Salts of Gold. — Gold forms the aurous ion $\overset{+}{Au}$, and the auric ion $\overset{+++}{Au}$. One of these carries one electrical charge, or is univalent, and the other carries three electrical charges, or is trivalent. These ions can form salts with the anions of certain acids.

EXPERIMENTS WITH COPPER AND SILVER

Experiment 187. Action of Reagents on Salts of Copper. — (Copper sulphate; sodium hydroxide; ammonium sulphide; hydrogen sulphide.)

To a cold, dilute solution of copper sulphate add sodium hydroxide. Cupric hydroxide is precipitated with a bluish color. Warm the solution; the color gradually changes to black. This is due to the loss of water and the formation of cupric oxide.

Pass hydrogen sulphide through a solution of copper sulphate. What occurs?

Add ammonium sulphide to a solution of copper sulphate. What is precipitated? Write equation?

Test the solubility of copper sulphide in dilute acids? (See page 298.)

Experiment 188. Copper precipitated from its Salts by Certain Metals. — (Copper sulphate; bar of zinc.)

File the surface of a bar of zinc to clean it, and plunge it into a solution of copper sulphate. Copper is deposited upon the zinc, and zinc passes into solution. The reaction that takes place is the following: —

$$\overset{++}{\mathrm{Cu}}, \overset{=}{\mathrm{SO}_4} + \mathrm{Zn} = \overset{++}{\mathrm{Zn}}, \overset{=}{\mathrm{SO}_4} + \mathrm{Cu}.$$

Zinc takes the positive charge from the copper, itself becoming an ion, while the copper having lost its charge becomes an atom, and is precipitated in the metallic condition. (See page 298.)

Experiment 189. Copper precipitates Certain Metals from their Salts. — (Strip of copper; mercuric chloride or nitrate.)

Dip a strip of copper into a solution of mercuric chloride or mercuric nitrate. Mercury is precipitated upon the copper, and some of the copper dissolves. The reaction that takes place is: —

$$\overset{++}{\mathrm{Hg}}, \overset{-}{\mathrm{Cl}}, \overset{-}{\mathrm{Cl}} + \mathrm{Cu} = \overset{++}{\mathrm{Cu}}, \overset{-}{\mathrm{Cl}}, \overset{-}{\mathrm{Cl}} + \mathrm{Hg}.$$

Copper takes the charge from the mercury, becoming an ion, while the mercury, having lost its charge, becomes an atom.

Experiment 190. Action of Reagents on Silver Nitrate. — (Silver nitrate; sodium hydroxide; potassium chloride, bromide, and iodide; ammonia; hydrogen sulphide.)

Treat silver nitrate with sodium hydroxide. What is formed? Is it soluble in an excess of sodium hydroxide?

Treat silver nitrate with potassium chloride. What is formed? Write the equation?

Treat silver nitrate with potassium bromide. What is precipitated? Write equation?

Treat silver nitrate with potassium iodide. What is the precipitate? Equation?

Test the solubility of silver chloride, bromide, and iodide in ammonia?

Pass hydrogen sulphide through a solution of silver nitrate. What is precipitated? Is it soluble in dilute acids?

Experiment 191. Action of Light on Silver Chloride and Silver Bromide. — (Silver nitrate; potassium chloride; potassium bromide.)

Precipitate some silver chloride. Preserve a part of it in the dark and expose the remainder to the light for a few hours. What difference do you notice in the two samples?

Precipitate silver bromide and preserve a part in the dark, exposing the remainder to the light. What visible effect is produced by the light? (See page 301.)

Experiment 192. Silver precipitated by Mercury. — (Silver nitrate; mercury.)

Dissolve 3 grams of silver nitrate in 100 cc. water. Place the solution in a narrow cylinder and add one or two drops of mercury. Silver will separate, and mercury will pass into solution. The reaction is expressed thus: —

$$\overset{+}{\mathrm{Ag}},\ \overset{-}{\mathrm{NO_3}} + \mathrm{Hg} = \mathrm{Ag} + \overset{+}{\mathrm{Hg}},\ \overset{-}{\mathrm{NO_3}}.$$

The mercury removes the charge from the silver, becoming an ion. The silver, having lost its charge, becomes an atom.

PROBLEMS

1. Amount of copper sulphate that can be formed from 5 grams of cuprite? How much zinc would be required to precipitate this amount of copper from solution?

2. From 8.4 grams of argentite how much silver could be obtained? How much silver chloride, nitrate, and sulphate can be formed from the above amount of silver?

3. Weight of gold which combines with 4 litres of chlorine to form gold trichloride? Weight of auric chloride formed from the above amount of gold?

CHAPTER XXV

LEAD, TIN

LEAD (At. Wt. = 206.9)

There remain two elements in group IV which have not been studied. These are tin and lead. Although the atomic weight of tin is less than that of lead, its chemistry is more complex, and it will be considered after lead.

Occurrence, Preparation, and Properties of Lead. — Lead occurs in nature in a number of compounds. The most important is the sulphide PbS, or *galena*.

Galena, being the principal ore of lead, is the one from which most of the lead of commerce is prepared. Several methods are employed to obtain the lead from the sulphide. One method is to roast the sulphide, converting it into the oxide, and then reduce the oxide with carbon: —

$$2\ PbS + 3\ O_2 = 2\ PbO + 2\ SO_2;$$
$$PbO + C = CO + Pb.$$

A second method is to roast the sulphide until a part of it is converted into the oxide, and then heat the oxide with the sulphide: —

$$PbS + 2\ PbO = 3\ Pb + SO_2.$$

The action of water upon lead is of hygienic importance. Pure water dissolves lead much more readily than ordinary impure water, such as that in springs, rivers, etc. The impurities react with the lead and form a coating of carbonate, sulphate, etc., which protects the metal from the further action of the water. If the water contains free carbon dioxide or organic acids, it acts upon the lead, converting it into the salt of the acid in question. The hygienic question is, whether drink-

ing-water should be conducted through lead pipes. All things considered, it is much safer not to use them, since pipes made of certain other metals are practically unacted upon by water.

Lead is readily precipitated from its salts by a number of metals. This is especially the case with zinc and iron. When a bar of zinc is suspended in a solution of a lead salt, the lead is thrown out and the zinc dissolves. What takes place is a transfer of the electrical charge from the lead ion to the zinc atom, converting the former into an atom and the latter into an ion: —

$$\overset{++}{Pb},\ \overset{-}{NO_3},\ \overset{-}{NO_3} + Zn = \overset{++}{Zn},\ \overset{-}{NO_3},\ \overset{-}{NO_3} + Pb.$$

Oxides of Lead. — Lead forms a number of compounds with oxygen. *Lead suboxide*, Pb_2O: *Lead oxide*, PbO, is also known as *litharge* or *massicot*.

Minium, or *red lead*, Pb_3O_4, is formed by gently heating lead oxide on the air (to 300°–400°).

Lead sesquioxide has the composition, Pb_2O_3.

Lead dioxide, PbO_2, is formed by oxidizing the lower oxides of lead by the action of nitric acid upon minium.

Chloride of Lead. — Lead generally forms the bivalent ion $\overset{++}{Pb}$, which readily combines with the anions of acids, forming salts that are beautifully crystallized.

Lead chloride, $PbCl_2$, is readily formed by bringing together lead ions, $\overset{++}{Pb}$, and chlorine ions, $\overset{-}{Cl}$: —

$$\overset{++}{Pb},\ \overset{-}{NO_3},\ \overset{-}{NO_3} + \overset{-}{Cl},\ \overset{+}{Na} + \overset{-}{Cl},\ \overset{+}{Na} = \overset{+}{Na},\ \overset{-}{NO_3} + \overset{+}{Na},\ \overset{-}{NO_3} + PbCl_2.$$

Lead chloride is a white, crystalline substance, somewhat soluble in hot water, but only slightly soluble in cold water.

Lead Sulphide, PbS, occurs in nature, as we have already seen, as *galena*. It is formed whenever bivalent lead ions come in contact with sulphur ions — whenever a soluble lead salt is treated with hydrogen sulphide: —

$$Pb(NO_3)_2 + H_2S = 2\,HNO_3 + PbS.$$

Lead Carbonate, $PbCO_3$. — The carbonate of lead is an important compound, and especially the basic carbonates. The

normal carbonate occurs in nature as *cerussite*, and is isomorphous with aragonite, a form of calcium carbonate. The normal carbonate is formed when ammonium carbonate is added to a solution of lead nitrate: —

$$Pb(NO_3)_2 + (NH_4)_2CO_3 = 2\,NH_4NO_3 + PbCO_3.$$

If any other alkaline carbonate is used, such as sodium carbonate, a *basic lead carbonate* is precipitated, and this is extensively used as a pigment under the name of *white lead.*

The old Dutch method of making white lead consists in placing sheet lead, rolled into spirals, in porcelain pots containing a little vinegar. The latter did not touch the lead. The vessels were then placed in horse-manure, which decomposed and furnished the necessary amount of carbon dioxide. The lead plates became covered in time with a layer of basic lead carbonate, which was removed mechanically.

This method, which consumed much time, has now given place to some extent to quicker processes. Normal lead acetate is shaken with litharge and water, when the basic acetate is formed. This is then treated with carbon dioxide, when basic lead carbonate is formed. The ordinary white lead which is used as a pigment is a mixture of basic carbonates of different composition.

Lead Acetate, $Pb(CH_3COO)_2 \cdot 3\,H_2O$, is an important soluble salt of lead. It is formed by the action of acetic acid on lead oxide or finely divided lead. On account of its sweet taste it is known as *sugar of lead.*

TIN (At. Wt. = 119.0)

An element chemically allied to lead, but differing from it in many respects, is tin. This metal is useful on account of its chemical inactivity, is valuable on account of its properties, and expensive because it does not occur in large quantities. Tin occurs in the uncombined condition along

with gold, but chiefly as tin dioxide, SnO_2, known as *tinstone* or *cassiterite*.

Preparation and Properties of Tin. — The sulphur, arsenic, and similar impurities are removed from the tin ore by roasting, and the oxide is then heated with carbon. The oxide is readily reduced to the metal, and this is purified by repeated melting, the molten tin being poured off from the less easily fusible alloys.

Tin is light in color and quite soft. It can be readily hammered or rolled into thin sheets known as tin-foil, which is used for covering objects to protect them from the action of air, moisture, etc. It is crystalline, and the movement of the crystals over one another produces a crackling noise known as the *cry of tin*.

Alloys of Tin. — Molten tin dissolves readily in most of the other metals in the molten condition, and forms a large number of alloys with them. Some of these are very important substances. *Soft solder* is an alloy of tin and lead. The *bronzes*, as has already been stated, are alloys of tin and copper.

The Tin Ions. — The element tin forms two kinds of ions, those which are bivalent, $\overset{++}{Sn}$, and those which are quadrivalent, $\overset{++++}{Sn}$. Of these the quadrivalent ion is the more stable, the bivalent tending to pass over into it. No other ion of tin is known. The stannous ions passing over into the stannic, readily take up two electrical charges, or are good reducing agents, as we say.

Stannous (SnO), and Stannic (SnO_2), Oxides. — The two oxides corresponding to the stannous and stannic conditions are known. *Stannous oxide*, SnO, formed by heating stannous hydroxide in a current of carbon dioxide, is comparatively unstable, readily combining with oxygen and forming stannic oxide, SnO_2. *Stannic oxide*, SnO_2, occurs in nature as *tin-stone*.

Stannous Hydroxides, $Sn(OH)_2$. — Stannous hydroxide is precipitated from stannous salts by the addition of an alkali: —

$$SnCl_2 + 2\,NaOH = 2\,NaCl + Sn(OH)_2.$$

Stannous hydroxide readily dissolves in an excess of the alkali, forming salts.

Stannic Hydroxide, $Sn(OH)_4$, is formed by treating tin with nitric acid of medium concentration. It readily loses water, forming *metastannic acid*, H_2SnO_3.

Stannous Chloride, $SnCl_2 . 2\,H_2O$. — The best-known stannous salt is the chloride, $SnCl_2$. It is formed by dissolving tin in hydrochloric acid, also by heating tin in a current of dry hydrochloric acid gas. It combines readily with chlorine, forming stannic chloride. So great is this power that it removes the chlorine from the chlorides of mercury, precipitating metallic mercury: —

$$2\,HgCl + SnCl_2 = 2\,Hg + SnCl_4;$$
$$HgCl_2 + SnCl_2 = Hg + SnCl_4.$$

Stannous chloride combines directly with free chlorine, forming stannic chloride: —

$$\overset{++}{Sn},\ \bar{Cl},\ \bar{Cl} + Cl_2 = \overset{++++}{Sn},\ \bar{Cl},\ \bar{Cl},\ \bar{Cl},\ \bar{Cl}.$$

Stannous chloride is known commercially as *tin-salt*.

Stannic Chloride, $SnCl_4$. — The tetrachloride is formed, as we have seen, by the action of mercurous or mercuric chloride on stannous chloride. It is also formed by the direct action of chlorine gas on tin. When brought in contact with a little water, it forms a viscous mass known as *tin-butter*, having the composition $SnCl_4 . 3\,H_2O$.

Sulphides of Tin. — Stannous sulphide, SnS, is formed by conducting hydrogen sulphide into a solution of stannous chloride: —

$$SnCl_2 + H_2S = 2\,HCl + SnS.$$

Stannous sulphide is a brownish black powder, insoluble in dilute acids, but soluble in ammonium polysulphide, forming ammonium *sulphostannate*, in which the tin is in the quadrivalent condition: —

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

Stannic sulphide is precipitated as a light yellow powder when hydrogen sulphide is passed into a solution of a stannic salt or a stannate: —

$$SnCl_4 + 2\,H_2S = 4\,HCl + SnS_2.$$

Stannic sulphide dissolves readily in ammonium sulphide, forming *sulphostannates* or *thiostannates*: —

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

This reaction is of importance in the separation of tin from most of the elements.

EXPERIMENTS WITH LEAD AND TIN

Experiment 193. Precipitation of Lead from its Salts by Other Metals. — (Lead nitrate or acetate; bar of zinc.)

Add a few grams of lead nitrate or acetate to a flask holding 2 litres of water and fill the flask with water, adding a drop or two of nitric acid. Suspend a bar of zinc in the solution of the lead salt. The lead will be gradually thrown out and deposited upon the zinc in arborescent forms, known as the *lead tree*.

Allow this to stand several days, and often beautiful results are secured. The zinc takes the electrical charges from the lead ions, converting them into atoms; while the zinc atoms, having received electrical charges, become ions and pass into solution. (See page 308.)

Experiment 194. Oxides of Lead. — (Litharge; minium; lead sesquioxide; lead dioxide.)

Compare the several oxides of lead with respect to their visible properties. Treat minium with dilute nitric acid. Is there any change in the appearance of the compound? Is it possible to dissolve minium completely in nitric acid? Filter the solution, preserving both the residue and filtrate. Test the filtrate for lead by passing in hydrogen sulphide?

Treat lead dioxide with a little hydrochloric acid and boil. What is given off?

Treat lead dioxide with hydrogen dioxide in the presence of a little nitric acid. Explain what takes place?

Perform these same experiments with the residue from minium? (See page 308.)

Experiment 195. Lead Chloride. — (Lead nitrate; sodium chloride.)

Treat a solution of lead nitrate with a solution of sodium chloride. White lead chloride is precipitated. Boil the solution, and filter hot. Test a little of the filtrate for lead by passing in hydrogen sulphide. Set the solution aside and allow it to cool. Lead chloride will separate in the form of crystals. Lead chloride is only slightly soluble in cold water, but much more soluble in hot water. (See page 308.)

Experiment 196. Lead Sulphide. — (Lead nitrate; hydrogen sulphide; ammonium sulphide.)

Add ammonium sulphide to a solution of lead nitrate. What is precipitated? Pass hydrogen sulphide through a solution of lead nitrate. What is precipitated? Is lead sulphide soluble in dilute acids? (See page 308.)

Experiment 197. Tin thrown down by Other Metals. — (Stannous chloride; bar of zinc.)

Suspend a bar of zinc in a solution of stannous chloride to which a few drops of hydrochloric acid have been added. Allow the zinc to stand in the solution for some days in a quiet place. What is formed?

Zinc takes the charge from the tin ions, converting them into atoms. The zinc, having become charged, passes into solutions as ions: —

$$\overset{++}{\mathrm{Sn}},\ \bar{\mathrm{C}}\mathrm{l},\ \bar{\mathrm{C}}\mathrm{l} + \mathrm{Zn} = \overset{++}{\mathrm{Zn}},\ \bar{\mathrm{C}}\mathrm{l},\ \bar{\mathrm{C}}\mathrm{l} + \mathrm{Sn}.$$

Experiment 198. Hydroxides of Tin. — (Stannous chloride; sodium hydroxide; tin; concentrated nitric acid.)

Add sodium hydroxide to a solution of stannous chloride. Stannous hydroxide is thrown down. Equation? Add an excess of sodium hydroxide. Does stannous hydroxide dissolve in an excess of sodium hydroxide? What is formed?

Treat a few grams of tin with a little concentrated nitric acid. Dense fumes are given off, and stannic hydroxide minus water, H_2SnO_3, is formed: —

$$\mathrm{Sn(OH)_4} - \mathrm{H_2O} = \mathrm{H_2SnO_3}.$$

This compound, which is a white, insoluble powder, is known as metastannic acid. (See page 311.)

Experiment 199. Preparation and Properties of Stannous Chloride. — (Tin; hydrochloric acid.)

Treat a piece of tin with hydrochloric acid and warm. Tin dissolves, and stannous chloride is formed.

Treat a little of the stannous chloride solution with a few drops of a solution of mercuric chloride. The mercuric chloride is reduced to white, mercurous chloride, which, being insoluble, is precipitated. Add more of the solution of stannous chloride and warm the solution. The reduction goes farther; the mercurous chloride being reduced to metallic mercury, which is thrown down as a black precipitate. (See page 311.)

Experiment 200. Sulphides of Tin. — (Stannous chloride; stannic chloride; freshly prepared ammonium sulphide; yellow sulphide of ammonium.)

Pass hydrogen sulphide into a solution of a stannous salt; also into a solution of a stannic salt. Stannous sulphide is thrown down in the former case and stannic sulphide in the latter.

Treat stannous sulphide with freshly prepared ammonium sulphide. Does it dissolve? Treat it with yellow sulphide of ammonium. Does it dissolve?

Treat stannic sulphide with freshly prepared ammonium sulphide. Does it dissolve? Treat it with yellow sulphide of ammonium. Does it dissolve? How would you distinguish a stannous from a stannic compound? (See page 311.)

PROBLEMS

1. Zinc required to precipitate 206.9 grams of lead from a solution of lead nitrate? What relation does this bear to the atomic weight of zinc?

2. Percentage of lead in each of the four oxides of lead?

3. Amounts of stannous and stannic chlorides that can be prepared from 1 gram of stannous oxide? from 1 gram of stannic oxide?

CHAPTER XXVI

I. RUTHENIUM	RHODIUM	PALLADIUM
II. OSMIUM	IRIDIUM	PLATINUM

Although classed together, these two groups of three elements each have certain properties which are markedly different. The most striking is the atomic weights. The first three have atomic weights which are not widely removed from one hundred, while the atomic weights of the last three are not widely removed from two hundred. Similarly, the specific gravities of the first three elements is close to twelve, while the specific gravities of the last three is about twenty-two.

These elements, however, all resemble platinum more or less closely, and are all comparatively rare; platinum itself not occurring in very large quantities.

The chemistry of these substances presents certain points of interest. Palladium absorbs large volumes of hydrogen gas, and it has been supposed for a long time, forms the compound Pd_2H, known as *palladium hydride.* There is some doubt at present as to whether this is a definite chemical compound.

Osmium combines with oxygen, forming the compound OsO_4. This compound is remarkable in that there is no element known which has the power to combine with *more than four oxygen atoms.*

PLATINUM (At. Wt. = 195.0)

Platinum, one of the most valuable elements from the standpoint of chemistry, on account of its power to resist chemical reagents, occurs fairly widely distributed, but not in large quantities. It occurs in company with the other platinum metals, and is separated from them by methods with which we are now more or less familiar.

Properties of Platinum. — Platinum is light in color, has a specific gravity of 21.4, and melts at about 1770° in the flame of the oxyhydrogen blowpipe. It is both ductile and malleable — can be drawn into thin wire and hammered into thin sheets.

Platinum can exist in a number of physical conditions. In addition to ordinary white platinum, which is very compact and metallic in all of its properties, we know platinum in the form of a spongy mass which is known as *platinum sponge.* Platinum is obtained in this condition when the chloride of ammonium and platinum, which will be referred to a little later, is heated. Platinum sponge has a gray color, and differs fundamentally from the black variety of platinum known as *platinum black.* This is obtained by reduction of platinum compounds. When both of these varieties are highly heated and subjected to pressure, they pass back into ordinary white platinum. Finely divided platinum has a remarkable power to absorb oxygen. It can absorb several hundred volumes of oxygen, and the oxygen in this condition is very active chemically, readily effecting oxidations. In a similar manner it can absorb considerable quantities of hydrogen, and the hydrogen under these conditions has strongly reducing properties.

This power of platinum to absorb gases, and to produce chemical combinations between them, can be readily illustrated by means of a piece of platinum foil and a gas-jet. Ignite the jet and heat the platinum to redness. Then extinguish the jet until the platinum ceases to glow. If now the gas-jet is turned on again and the gas allowed to flow over the surface of the hot, but not incandescent, platinum, it will be reignited. This experiment can be repeated as often as desired with the same piece of platinum.

The power of platinum to absorb gases and produce chemical reaction catalytically, is also illustrated by a *form of lamp devised by Davy.*

An ordinary spirit lamp is filled with a mixture of alcohol and ether, and ignited. A spiral of platinum wire is suspended in the flame and heated to incandescence. The flame is then

extinguished until the spiral ceases to glow. If the vapors of alcohol and ether are now allowed to fall again on the hot platinum, the latter will again become incandescent and ignite the lamp.

The *Döbereiner lamp*, constructed early in the nineteenth century, is based upon the same principle. A current of hydrogen is allowed to flow over spongy platinum, when it combines so rapidly with oxygen that the platinum is heated to incandescence and ignites the hydrogen.

Chemically, platinum is very resistant to reagents, and upon this fact its value chiefly depends. It is not attacked appreciably by any of the strong mineral acids, but dissolves in aqua regia. It, however, dissolves in the fused alkalies, cyanides, etc. Platinum must not be heated in contact with carbon, since some of the carbon dissolves and makes the platinum brittle.

Uses of Platinum. — Platinum is especially useful to the chemist on account of its resistance to chemical reagents. It is not attacked appreciably even by hydrofluoric acid. It is also not attacked by the fused alkaline carbonates. Platinum vessels can thus be used where even porcelain could not be employed. On account of its high melting-point platinum is used for holding substances which are to be heated to a high temperature. Since it does not volatilize in the flame of the bunsen burner, it does not impart any color to the flame, and is therefore useful in spectrum analysis to hold the substance whose spectrum it is desired to study. A platinum wire is made into a loop and dipped into the substance in question. It is then inserted into the flame, when only the spectrum characteristic of the substance appears.

Platinum finds to-day extensive applications in the arts. Platinum has nearly the same temperature coefficient of expansion as glass, and almost exactly the same as red and blue fusion glass. If it is desired to seal an electrical connection through glass, a platinum wire is the most convenient means. This fact is utilized not only in constructiug standard

cells, but also incandescent electric lights. Large amounts of platinum are used in this way.

Oxides and Hydroxides of Platinum. — Platinum forms two oxides, PtO and PtO_2, which are derived from the corresponding hydroxides, $Pt(OH)_2$ and $Pt(OH)_4$, by careful heating. The hydroxides are obtained from the platinous and plantinic chlorides, or from the double chlorides with the alkalies, by the action of a base. All of these substances are unstable at elevated temperatures, breaking down and yielding metallic platinum.

Chlorides of Platinum. — Platinum forms two chlorides, — platinous chloride, $PtCl_2$, in which the platinum is bivalent, $\overset{++}{Pt}$, and plantinic chloride, in which the platinum is tetravalent, $\overset{++++}{Pt}$. Platinic chloride, which is quite soluble in water, readily combines with hydrochloric acid, forming *hydrochlorplatinic acid*, H_2PtCl_6. This same compound is formed when platinum is dissolved in aqua regia.

Many salts of this acid are known. The potassium and ammonium chlorplatinates, K_2PtCl_6 and $(NH_4)_2PtCl_6$, are difficultly soluble in water, while the sodium salt, Na_2PtCl_6, is readily soluble. This reagent thus enables us to separate sodium from potassium.

In this acid the chlorplatinic ion, $\overset{=}{PtCl_6}$, is bivalent, and this is an example of a metal forming part of an anion. When a solution of this acid is electrolyzed, the platinum passes to the anode and not to the cathode.

CHAPTER XXVII

GENERAL RELATIONS

RELATIONS WITHIN THE GROUPS OF THE PERIODIC SYSTEM

Group I. — The chemical relations between sodium and potassium are very close indeed. These elements have the same general properties and show the same reactions towards water and other reagents. The hydroxides are both univalent, and are the strongest bases. The salts with all of the more common acids are surprisingly similar, and these elements are as closely allied as any two of the more common elements in the whole field of chemistry.

Sodium and potassium are also very closely allied to the rarer elements, lithium, rubidium, and cæsium.

Copper, silver, and gold, while bearing many relations to one another, differ markedly and in many respects from the alkali metals just considered. Copper may be univalent and bivalent, and gold univalent and trivalent. These substances are not such strong base-forming elements as the alkalies. Indeed, the power to form acids begins to manifest itself in gold.

Group II. — Calcium, strontium, and barium are very closely allied. Indeed, about as closely as sodium and potassium. These elements all decompose water, forming strong bases. They are all bivalent, and their compounds with the different acids are strikingly alike. These compounds may differ in their solubility in certain solvents, but, in general, when one of the alkaline earths forms a difficultly soluble salt with an acid, the corresponding salts of the other two elements are difficultly soluble. Magnesium, zinc, cadmium, and mercury are more closely allied to each other than to calcium, strontium,

and barium. Magnesium, however, resembles the calcium group much more closely than the others.

Zinc is always bivalent, but its hydroxide is both basic and acidic, depending upon conditions. Its sulphide is insoluble in water, and thus differs from all preceding elements. Cadmium is nearly always bivalent, but can act as a univalent element, while mercury is both univalent and bivalent.

Group III. — The first element, boron, is a strongly acid-forming element, while aluminium in its hydroxide is both base-forming and acid-forming. These elements are both trivalent. The remaining elements of this group are comparatively rare substances.

Group IV. — Carbon and silicon are closely allied in many respects. They are both quadrivalent in most of their reactions, and are both markedly acid-forming elements. Both form homologous series of compounds, and their chemistry is, therefore, comparatively complex.

Tin and lead, the remaining two abundant elements in this group, differ markedly from the first two, but show certain not very close relations to one another. Tin is bivalent and quadrivalent, while lead is bivalent. The hydroxides of both of these elements are both basic and acidic, depending upon conditions. They are both well-characterized metals, while carbon and silicon are pronounced metalloids.

Group V. — The relationships in group V are very satisfactory, at least as far as the well-known elements nitrogen, phosphorus, arsenic, and antimony are concerned. The elements in this group have variable valence, but are generally trivalent or pentavalent. They are all acid-forming elements, but most of them can combine with strong acids and form salts. The compounds of these several elements with hydrogen, and with hydrogen and oxygen, are strikingly alike in their properties. Their compounds with chlorine also closely resemble each other.

Bismuth, which has the highest atomic weight of any member of the series, shows basic properties.

Group VI. — Here the familiar elements oxygen and sulphur,

and the rarer elements selenium and tellurium have many points of resemblance. Their compounds with hydrogen have strictly analogous composition. They are all strongly acid-forming elements, and all except oxygen have a valence as high as six.

The remaining three elements in this group are comparatively rare substances, and cannot be brought within the scope of this work.

Group VII. — The relationships here between fluorine, chlorine, bromine, and iodine are as close or closer than in any other group. Their compounds with hydrogen, with hydrogen and oxygen, with the metals and non-metals in general, show surprisingly close relations. They are among the strongest acid-forming elements, and have a maximum valence of seven.

The relation of manganese to the halogens is not so obvious. There are certain analogies between the compounds of manganese and those of the halogens. Thus, permanganic acid resembles in composition perchloric acid, the manganese having a valence of seven. If, however, we consider in a broad way the chemistry of manganese, we shall find it much more closely allied to iron and chromium than to the halogens, and it is a weak point in the Periodic System that it should fall in group VII.

Group VIII. — This group contains those elements which are usually not regarded as fitting into the system. Certain close relations, however, exist between the several sub-groups of three elements within this group.

Iron, cobalt, and nickel show many relations both in the elementary condition and in their hydroxides and salts.

The rare elements ruthenium, rhodium, and palladium are also closely allied; while osmium, iridium, and platinum are among the most closely allied of the chemical elements. Even within this overflow group we have, then, many unquestionable relations manifesting themselves.

RELATIONS BETWEEN THE COMPOUNDS OF THE METALS

Oxides. — The oxides of the metals, with the exception of the alkalies, are difficultly soluble in water. The oxides of the alkaline earths are somewhat soluble in water. Indeed, most of the oxides are practically insoluble, and occur in nature as valuable ores. This is the case especially with aluminium, iron, manganese, and the like.

Hydroxides. — The hydroxides of the metals, with the exception of the alkalies, are generally difficultly soluble in water. This has been shown by repeated experiments in which the hydroxides of the heavy metals were formed by treating the soluble salts of the metals with a soluble hydroxide. The hydroxides of the alkaline earths are somewhat soluble in water — barium being the most soluble and calcium the least.

Certain of the hydroxides, like zinc, aluminium, and lead, are of special interest in that they act as bases towards the strong acids, and as acids towards the stronger bases. The basic nature of the hydroxides is most pronounced with the alkalies, and becomes less and less as we pass to the right in the Periodic System, as has already been pointed out.

Halides. — The halides of the metals include the chlorides, bromides, iodides, and fluorides. They are formed by dissolving the metal, the oxide, or the carbonate in the acid in question. The chlorides are formed by treating soluble sulphates with barium chloride. Write the equations in each case?

The chlorides of most of the metals are soluble in water. *Silver* and *mercurous* chlorides are exceptions. *Lead* chloride is quite soluble in hot water, but soluble with difficulty in cold water. These facts are important, as we shall see, in connection with the qualitative separations of the metals.

Nitrates. — The nitrates of the metals are formed by dissolving the metal, the oxide, or the carbonate in nitric acid. Also by treating soluble sulphates or carbonates with the nitrates of

elements which form insoluble sulphates or carbonates. Thus, when sodium sulphate is treated with barium nitrate, barium sulphate is precipitated and sodium nitrate remains in solution.

The nitrates of all the metals are soluble in water. These easily give up oxygen at elevated temperatures and are, therefore, good oxidizing agents.

Sulphates. — The sulphates are formed by the solution of metals, oxides of the metals, or carbonates of the metals in sulphuric acid. When the sulphate is insoluble, it is formed by treating a soluble salt of the metal with a soluble sulphate, or with sulphuric acid. The sulphates of the alkalies are fairly soluble, but are not to be classed among the very soluble compounds. The sulphates of the alkaline earths are very insoluble substances. Calcium sulphate, to be sure, dissolves slightly in water, but strontium sulphate is less soluble, and barium sulphate one of the most insoluble compounds known in the whole field of chemistry.

All degrees of solubility are represented among the sulphates of the heavy metals. In general, they are more soluble than the sulphates of the alkaline earths.

Carbonates. — Since carbonic acid is so weak and is volatile, the carbonates cannot be prepared by dissolving the metal or its compounds in a solution of carbonic acid. The carbonates are prepared by passing carbon dioxide through a solution of the hydroxide of the metal in question. Also by the action of a soluble carbonate on a solution of a salt of the metal.

The carbonates of the alkalies are soluble. The carbonates of the other elements are insoluble. Some of the carbonates occur in nature in large quantities. This is especially true of the carbonates of calcium and magnesium. The acid carbonates are often more soluble than the carbonates.

The carbonates of the metals are decomposed by heat, yielding carbon dioxide which is volatile, and the oxide of the metal. The temperature required varies greatly from one carbonate to another.

Phosphates. — The phosphates are formed when soluble salts of the metals are treated with a solution of a soluble phosphate; *e.g.* with disodium phosphate. The normal phosphates of all of the metals, with the exception of the alkalies, are insoluble in water. The secondary and primary phosphates may differ greatly from the normal phosphate in solubility. Such is the case with the various phosphates of calcium. Some of the phosphates occur in nature as minerals.

Sulphides. — The sulphides are specially interesting in connection with the qualitative separations of the metals from one another. There are some metals whose sulphides are soluble in water; others whose sulphides are soluble in dilute acids; others again whose sulphides are insoluble in dilute acids; and still others whose sulphides dissolve in ammonium polysulphide. Upon these facts is based the division of the elements, from the standpoint of qualitative analysis, into several groups.

Group I includes those elements whose chlorides are insoluble in water, and which are, therefore, precipitated from solutions of their soluble salts by soluble chlorides or hydrochloric acid. These include *silver*, *lead*, and *mercurous mercury*.

Leaving group I, or those metals whose chlorides are insoluble in water (lead, silver, and mercurous mercury), we come to *Group II*, or those elements whose sulphides are precipitated by hydrogen sulphide in the presence of dilute acid, and whose sulphides are soluble in the polysulphides of ammonium. These are *arsenic*, *antimony*, and *tin*, and also *gold* and *platinum*.

Group III includes those elements whose sulphides are precipitated by hydrogen sulphide in the presence of a dilute acid, and whose sulphides are insoluble in ammonium polysulphides. These include *cadmium*, *mercury*, *copper*, *lead*, *silver*, and *bismuth*.

Group IV includes those metals whose sulphides are not precipitated by hydrogen sulphide, since their sulphides are

soluble in dilute acids, but are precipitated by ammonium sulphide either as sulphides or hydroxides. The members of this group are *iron*, *cobalt*, *nickel*, *zinc*, and *manganese*, which are precipitated as the sulphides; and *aluminium* and *chromium*, which are precipitated as the hydroxides.

Group V contains those elements whose sulphides are not precipitated by ammonium sulphide, but whose solutions are precipitated by a soluble carbonate. These are *calcium*, *barium*, *strontium*, and *magnesium*.

Group VI contains the alkalies: *sodium*, *potassium*, and *ammonium*. On account of the solubility of their salts they are not precipitated from their solutions by any of the ordinary reagents. To precipitate them, such reagents as platinic chloride, perchloric acid, tartaric acid, etc., are required.

Separation of the Members of Any Group. — To separate the individual members of any group from one another, special reactions characteristic of the elements in question must be used. It would lead too far to give a complete scheme of qualitative analysis in this place, and any scheme which is not complete is not satisfactory. In this connection reference must be had to some one of the many excellent works on qualitative analysis.

THE NATURE AND RÔLE OF IONS IN CHEMISTRY

We can see from what we have learned that the metals in general form cations, while the acid radicles form anions. A chemical compound is formed by the union of an anion with a cation. In some cases the metal, instead of forming a cation, unites with other elements forming part of the anion, as platinum in potassium platinum chloride. It is, however, a very simple matter in general to determine at a glance which constituent of a compound is the cation and which the anion. The most positive constituent, or strongest base-forming element, as it is said, is the cation, and the remainder of the compound the anion.

We thus see that the cations of compounds are in general very simple, being in most cases atoms of the metals; while the anion may be simple, as the anion of hydrochloric acid $\bar{Cl}$, or may be, and usually is, complex, as the anion of sulphuric acid, $\bar{\bar{S}}O_4$.

The importance of the ions in chemistry has come to be recognized in the last few years. It is now quite certain that most reactions in inorganic chemistry are reactions between ions, molecules as such having nothing to do with the reaction. The molecules dissociate, yielding the ions, which then enter into chemical reaction. Some little of the evidence leading to this conclusion, which is of fundamental importance for the whole science of chemistry, has already been referred to. For a fuller discussion of this and similar subjects, larger works must be consulted.

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